A STUDY OF THE ACTION OF CARBON DIOXIDE ON THE BORATES OF BARIUM, AND OF THE ACTION OF ACID BORATES ON THE CARBONATE OF BARIUM AT HIGH TEMPERATURES.

DISSERTATION

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by

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A Study of the Action of Carbon Dioxide on the Borates of Barium, and of the Action of Acid Borates on the Carbonate of Barium at High Temperatures.

INTRODUCTION.

A method for the separation and determination of boric acid was devised in this laboratory, in 1888, by Morse and Burton, and published* by them with the results of twenty two determinations made in accordance with it. Essentially, the method is as follows:- "If the boric acid is in solution, the liquid containing it is made slightly alkaline with caustic potash, and evaporated on a water-bath", to a small volume. If the material containing the boric acid is not soluble in water, a silicate for example, a solution is effected by fusing it with caustic potash in a nickle crucible. The solidified mass is extracted with hot water, filtered and evaporated on a water-bath to a small volume. This concentrated solution treated with a drop of tropaeolin 0 0 (or methyl orange) which is not sensitive to boric, carbonic and silicic acids, is neutralized with dilute sulphuric acid. This converts any oxides or hydroxides

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* American Chemical Journal X, pp. 154 - 158.

present into sulphates, and frees the boric, carbonic and silicic acids. Enough dehydrated copper sulphate is now added to absorb the water and dehydrate the silicic acid, the mass transferred to a simple extraction apparatus and extracted with absolute alcohol. Boric acid alone, being soluble, is thus extracted from the mass. The extraction apparatus terminates beneath the surface of an aqueous solution of barium hydroxide in which there is present an excess of the base; this solution is contained in an Erlenmeyer flask protected fro the air during the extraction. Enough absolute alcohol is used in the extraction to furnish in the flask a mixture containing about 75% its volume of alcohol. "The excess of barium hydroxide is precipitated by passing into it a current of carbon dioxide, the contents of the flask are transferred to a weighed platinum dish, evaporated to dryness and heated to constant weight over a triple burner. The quantity of boric anhydride is found by the following proportion.

Mol. weight of B_2O_3 - mol. weight of CO_2 : mol. weight of B_2O_3 :: weight found - theoretical weight of the Ba as carbonate : weight of B_2O_3 found.

In 1898 the results of attempts to repeat this method, made in the Kent Laboratory (Yale) by L. C. Jones, were

published.* Parts of this article will be quoted:-
"To a measured amount of (aqueous) boric acid solution an excess of barium hydroxide was added, carbon dioxide passed and the whole evaporated", and subjected to successive "ignitions" to bring it to a constant weight. Such was not obtained; but deficits in weight amounting in one case to as much as 64% of the weight of boric acid originally present. "Plainly the results vary with the degree of ignition. This is obviously natural if the carbon dioxide acts on the barium borate as well as on the excess of barium hydroxide; for it is to be expected that in the evaporation more or less of the free boric acid will volatilize and that in the subsequent ignition the boric acid remaining will tend to recombine more or less completely, replacing carbon dioxide." "It is plain that barium metaborate is decomposed in solution by carbon dioxide. The possibility remained that the carbon dioxide might be so regulated as to leave the metaborate unattacked." In experiments where it was attempted to regulate the carbon dioxide, the materials after ignition showed deficits in weight amounting to 8% and 20%, respectively, of the weight of boric acid originally present in each.

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* American Journal of Science, 4th Series, V, pp. 443-446.

A cursory examination of the results obtained by L. C. Jones leads one to think them contradictory to those obtained by Morse and Burton. But a comparison of the conditions under which each set of results was obtained brings some facts worthy of consideration to the front:

Before passing carbon dioxide, Morse and Burton had their borate and hydroxide in the presence of a 75% alcohol, and when carbon dioxide was conducted into the flask, it was their intention to continue this as long as was necessary for the neutralization of the excess of barium hydroxide. I have learned, though it is not stated in their article, that the heatings, after evaporation, were as gentle as was conformable with the purpose of driving out the last traces of alcohol and water; a triple burner was used, because of the large flame given, to facilitate uniformity of heating in all parts of the platinum dish.

Jones, before passing carbon dioxide, had his borate and hydroxide in the presence of water and in but two of his experiments was attention given to any regulation of the amount of carbon dioxide used. His results indicate, as will be shown later, the probability this his "ignitions" were of considerable length and intensity.

An article by Berg* bears upon this matter. It describes experiments showing that when an equivalent of B_2O_3 is treated with 1, 1 1/2, 2, 3, or 3 1/2 equivalents of B a O - both in aqueous solutions - and to the resulting solution an equal volume of 95% alcohol is added, one and the same salt, $BaB_2O_4 + 4\ H_2O$ is always obtained, and in crystalline form after one or two days standing. For the solution of one part of this salt 55000 parts of 75% alcohol are required. From this and from the recorded results of Morse and Burton, the most probable view to be taken is

(1) that metaborate of barium is formed during the proper manipulation of their method, and

(2) that, if attacked when in solution by carbon dioxide, it can not be appreciably attacked when it is removed from the sphere of action by virtue of its insolubility in 75% alcohol, in which it is more insoluble than barium carbonate in water.[1]

The following experiment, translated from Berg's article is also of interest, here:- "25 C C of boric acid solution and 75 C C of baryta water were mixed. There was present 1 atom of B_2O_3 to 1 1/2 atoms of B a O. In

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* Zeitschrift für analytische Chemie XVI pp.25-33.

(1) Zeitschrift für physikalische Chemie XII p. 125.

this case the precipitate first formed completely redissolved in the excess of baryta water. I convinced myself that the baryta water, and not the greater mass of water alone, accomplished the solution, by adding to a mixture of 25 C C of boric acid solution and 50 C C of baryta water 25^{cc} of water; the precipitate would not completely redissolve under these conditions." From this and from a study of Jones's article the most probable view to be taken is that there is no reason for supposing that in his experiments before the passage of carbon dioxide he had present any barium metaborate, while there is reason for thinking that he had present borates containing a larger proportion of base to acid than the metaborate. That such and also the metaborate should be decomposed by carbon dioxide when <u>in solution</u> would not be surprising; but such a decomposition does not necessitate, or in the absence of other data, warrant the assumption that in it boric acid, as such, is freed.

The first question that it was thought best to investigate was whether, during the evaporation which is subsequent to the passage of the carbon dioxide and which precedes the "ignitions", any B_2O_3 is volatilized, and if so, how much. Part I of this dissertation has to deal with this investigation.

PART I.

If, in attempting to precipitate an excess of barium hydroxide as carbonate in the presence of barium borates by passing carbon dioxide through the mixture while partially in suspension and partially in solution in some solvent, barium borates are decomposed giving free boric acid, this will volatilize more or less during the subsequent evaporation of the solvent. Therefore, by collecting and condensing the vapors given off during such an evaporation and ~~by~~ testing the distillates thus obtained, we have a means of determining how much, if any, boric acid has been volatilized during the evaporation. By varying the amounts of carbon dioxide used, and the character of the solvent other facts of interest may be gathered.

In the experiments described in this part, barium hydroxide and boric acid in solution were introduced into a retort. This retort was joined with a condenser and receiver; the solvent was distilled from a water bath, a current of some gas running through the apparatus constantly to facilitate the removal of the vapors as formed, to the condenser. This method of experimenting is, however, subject to the difficulty arising from "mechanical carrying over" of liquid or solid particles with the va-

pors in their passage from retort to receiver. The existence of the Wurtz, Hempel, Linnemann, Le Bel-Henninger and other special apparatus for distillations argues that this difficulty is considerable.

The limit to which the observer could rely upon the alcohol flame test for boric acid was fixed experimentally. Green could just be detected in burning 1 cc. of absolute alcohol containing in solution about .00007 grams B_2O_3, and then only at the instant before the flame died out. It was believed, hence, that the test was reliable so long as B_2O_3 was present to the extent of 7 parts in 80000 by weight, (taking the specific gravity of the alcohol as 0.8).

The sixteen experiments recorded in the table which follows were carried out, in general, thus: A measured volume of standard aqueous solution of barium hydroxide was introduced into the retort, and after it a measured volume of a solution of boric acid in absolute alcohol. Before beginning a distillation, in all cases, except the first four, enough alcohol was introduced to make the liquid in the retort a 50% alcohol, by volume. After joining up the apparatus the distillation was begun by heating upon a water-bath; then a stream of carbon dioxide

was conducted through the apparatus and maintained throughout the distillation.

To the residue in the retort more alcohol was added and the distillation repeated without interruption of the current of carbon dioxide. This treatment of the residue in the retort with alcohol, with subsequent evaporation was repeated four times with each charge of $Ba(OH)_2$ and B_2O_3 introduced into the retort.

use names

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Results of tests
	grams	grams		cc	%	cc	%		
I a	.6909	.1006	3 : 1	45.5	65.2	40.	72.	CO_2	negative
I b	.6909	.1006	3 : 1				82.	CO_2	negative
I c	.6909	.1006	3 : 1				92.	CO_2	positive
I d	.6909	.1006	3 : 1				96	CO_2	positive
II a	.6907	.1013	3 : 1	73.7	50.	52.	68.	CO_2	negative
II b	.6907	.1013	3 : 1	73.7	50.	50.	64.5	CO_2	negative
II c	.6907	.1013	3 : 1	114.	50.	54.	68.	CO_2	negative
II d	.6907	.1013	3 : 1	81.2	50.	52.		CO_2	negative
III a	.6839	.1012	3 : 1	80.	50.	50.5	75.6	CO_2	negative
III b	.6839	.1012	3 : 1	80.	50.	52.	74.3	CO_2	negative
III c	.6839	.1012	3 : 1	80.	50	51.1	72.6	CO_2	negative
III d	.6839	.1012	3 : 1	80.	50.	50.5		CO_2	negative
IV a	.6839	.1006	3 : 1	80.	50.	51.	74.	CO_2	negative
IV b	.6839	.1006	3 : 1	80.	50.	51.5	69.5	CO_2	negative
IV c	.6839	.1006	3 : 1	80.	50.	53.	64.5	CO_2	negative
IV d	.6839	.1006	3 : 1	80.	50.	51.	71.	CO_2	negative

Four more distillations were now made, the distillates tested as in the sixteen preceding cases, and then evaporated to dryness with caustic potash and tested again, with the addition of sulphuric acid and absolute alcohol. In the tests by the former method, negative results were gotten in all four cases, while by the latter method two negative and two positive tests were gotten. The following table gives the details, the general method being the same as in the first sixteen distillations.

[illegible]	Weight of BaO in retort	Weight of B_2O_3 in retort	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	Results of tests
	grams	grams		cc	%	cc	%		
V a	.6856	.1008	3 : 1	80	50	51.2	75	CO_2	negative
V b	.6856	.1008	3 : 1	80	50	51.2	73	CO_2	negative
V c	.6856	.1008	3 : 1	80	50	51.2	74	CO_2	positive
V d	.6856	.1008	3 : 1	80	50	50.9	72	CO_2	positive

It appears that traces of boric acid may have escaped detection in the tests in the first sixteen experiments.

It became evident that all work projected or in progress not bearing directly upon either the work of Morse and Burton, or of Jones, would have to be deferred; atten-

tion was therefore turned from work in 50% alcohol to work in water under conditions similar to those maintained by Jones during his evaporations.

Turmeric paper was prepared, as directed by Fresenius, for use in testing aqueous distillates for boric acid. To fix the limit of the turmeric test , aqueous solutions of boric acid of known strength were prepared, just enough hydrochloric acid being added to give an acid reaction toward methyl-orange indicator. A solution containing in equal volumes the same amount of hydrochloric acid, but not containing any boric acid, was prepared. Whenever a test was to be made, a slip of turmeric paper was taken from the glass stoppered jar well covered with black paper, in which it was kept, cut into halves, one half dipped into the solution to be tested for boric acid, and the other half for the same length of time into some of the dilute solution of hydrochloric acid. In testing very dilute solutions of boric acid where once dipping of the paper failed to indicate the acid present, more frequent dippings were resorted to. After each dipping the paper was dried on a glass plate heated upon a water bath. The concentration of the coloring matter on the edge of the wet portion of the papers rendered tests involving five or more dippings doubtful.

It was found that the turmeric test was unexpectedly delicate. Paper dipped once indicated B_2O_3 so long as it was present in amounts not less than 1 part in 59000 parts of water; dipped four times it indicated B_2O_3 so long as it was present in amounts not less than 1 part in 143000 parts of water. That is, it is a little more than ten times as delicate a test for boric acid in aqueous solution, as is the alcoholic flame test for boric acid in solution in absolute alcohol.

In the twenty distillations already described, evaporation of the material in the retort to dryness was never accomplished. This was desirable in the distillations ~~yet~~ to be described. To this end, a porcelain tube filled with broken porcelain and heated in a combustion furnace was and so arranged ~~and~~ joined with the retort by a tube through its tubulus, that by exhausting the receiver it was possible to have a current of hot dry air enter the retort, thus facilitating the distillation and making evaporation to dryness upon a water-bath possible. As is usually the case in using a porcelain combustion tube, it was found almost impossible to so protect either a cork or rubber stopper used in the end of the tube nearer the retort, as to prevent its burning. Finally the end of the tube was closed by baking into it a plug made of

a dough of firebrick clay, soluble glass, and water. A glass tube ran through the center of this plug. This proved so efficient and satisfactory that it is recommended in cases where the difficulty mentioned is encountered.

The five experiments in the following table were conducted, in general, thus:- Known volumes of aqueous barium hydroxide and boric acid solutions were brought into the retort. A drop of phenolphthalein indicator was added and carbon dioxide passed through the mixture to neutral reaction, and a minute or two longer. The retort was now put on a water-bath, joined with the combustion tube at its tubulus and with the condenser and receiver as usual. A Bunsen pump served to draw the hot air through the system, until the material in the retort came to dryness.

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[illegible]	Weight of BaO in retort	Weight of B_2O_3 in retort	Approximate ratio of BaO & B_2O_3 in retort	Volume of liquid in retort before distillation was begun	[illegible]	Volume of distillate collected and tested.	[illegible]	Atmosphere in which the distillation was conducted	[illegible]	Result to
	grams	grams		cc		cc				
VI	.1776	.0430	2 : 1	13.8	0	13.8	0	dry air	3	posit
VII	.1908	.0465	2 : 1	14.8	0	14.8	0	dry air	5	"
VIII	.1808	.0458	2 : 1	14.6	0	14.6	0	dry air	3	"
IX	.1903	.0458	2 : 1	14.7	0	14.7	0	dry air	4	"
X	.3806	.0467	4 : 1	22.3	0	22.3	0	dry air	4	"

While the apparatus was arranged, three experiments in 50% alcohol were tried. They differed in this respect alone from the five just described, and from the first twenty experiments, in that the amount of carbon dioxide used was but slightly in excess of that required to bring about neutral reaction toward phenolphthalein indicator. The results are recorded:

number of experiment	weight of BaO in retort	weight of B_2O_3 in retort	approximate ratio of BaO to B_2O_3 present in retort	Volume of liquid in retort before distillation began	Concentration of liquid in retort with respect to alcohol present	Volume of distillate collected and tested	Concentration of distillate with respect to alcohol present	atmosphere in which the distillation was conducted	number of times of dipping	Results of tests
	grams	grams		cc	%	cc	%			
XI	.2098	.0447	2 : 1	13.5	50	13.5	50	dry air	3	positive
XII	.4196	.0893	2 : 1	27.	50	27.	50	dry air	2	"
XIII	.4196	.0451	4 : 1	21.	50	21.	50	dry air	2	"

Experiments to determine the limit of the turmeric test as applied to solutions of boric acid in 50% alcohol had been carried ~~as~~ far enough ~~as~~ to show its ready application where there was at least 1 part of B_2O_3 present in 14000 parts of 50% alcohol, when all the solutions and carefully calibrated measuring apparatus were destroyed

by a fire. Upon what experience I had had with it before this, in my opinion it is very sensitive when thus applied. Too frequent dipping must ~~here~~ be avoided, however, because of the solubility of the coloring matter in the alcohol.

Conclusions:-

The question proposed for investigation in this part of the work was whether, during the evaporation ~~which is~~ subsequent to the passage of carbon dioxide, and before ~~and which precedes~~ the "ignitions", any boric acid is volatilized, and if so, how much.

As experiments I a to V d and XI, XII and XIII bear upon an unfinished problem, the discussion of them will be taken up after that of experiments VI to X.

Reference to the tables shows that in experiments VI to X the liquid in which the barium borate and carbonate were precipitated was water; that the carbon dioxide was restricted by aid of an indicator; and that in general the conditions were the same as those used by Jones in his two experiments where an attempt was made to restrict the amount of carbon dioxide used. In these he found deficits in weight after ignition of 8% and 20% of the total weight of B_2O_3 present, and amounting to errors of 1.9% and 5.2% when compared with the theoret-

ical weight for a mixture of barium carbonate and barium metaborate he expected to get. In the distillates gotten in experiments VI to X, knowing very closely the sensitiveness of the turmeric test and the volumes of the distillates we can approximate very closely to the total amounts of B_2O_3 present in them. Calculations upon this data have been made and, as applied to the extreme case among the five, will be given in order to avoid any misunderstanding.

Turmeric paper dipped 1 time indicates 1 part B_2O_3 in 59000 of water

Turmeric paper dipped 4 times indicates 1 part B_2O_3 in 143000 of water

assuming the gradation from 1 to 4 times as regular, then,

Turmeric paper dipped 2 times indicates 1 part B_2O_3 in 87000 of water

Turmeric paper dipped 3 times indicates 1 part B_2O_3 in 115000 of water.

Study of the table shows that in X the maximum amount of boric acid has appeared in the distillate. Its volume was 22.3 ^{cc} and the fourth dipping showed boric acid $22.3 \div 143000 = .00016^{g} B_2O_3$. The total B_2O_3 in it, therefore, was about $.00016^{g}$.

By further examination of the table and data derived from it, it was found that in experiment VI more

boric acid had appeared in the distillate in proportion to the theoretical weight of the B a O and B_2O_3 in the form of B a B_2O_4 and B a C O_3, than in any other of these five experiments. The theoretical weight referred to amounts to .2432^g and to find the B_2O_3 in the distillate we divide its volume by the test number for three dippings:-

$$13.8 \div 115000 = .00012^g B_2O_3$$

Calculation for percentage:-

$$\frac{100. \times .00012}{.2432} = .049 \%$$

That is, in the <u>maximum</u> or extreme case the error introduced into the final weighing by the loss of B_2O_3 during evaporation approximates to only about .049% of the total weight.

This answers the question which we started out to investigate:- The amount of boric acid appearing in any distillate after evaporation, when the previous treatment with carbon dioxide has been restricted, is, at its greatest, very small.

So small is this quantity that, in all fairness, it can as well be ascribed to the "mechanical carrying over" as to any decomposition of barium borate by the carbon dioxide used.

If this is the maximum amount of boric acid lost as a result of the decomposition of barium borates by carbon dioxide in the presence of water in which they are fairly soluble, how slight must be the boric acid lost as a result of the decomposition of barium metaborate by carbon dioxide in the presence of 75% alcohol in which it is, as has been pointed out, practically insoluble.

It was under these latter conditions that Morse and Burton worked, and their results indicate as does this work, that they did not suffer appreciably by loss of boric acid during evaporation.

Since it has been shown that under conditions analogous to those under which Jones worked only .00016^g B_2O_3 was lost during evaporation, amounting to only .35% of the total B_2O_3 present, it seems that Jones must be in error in ascribing greater losses than this to losses of boric acid by volatilization during evaporation.

Before closing Part I mention must be made of the experiments I a to V d and XI, XII and XIII.

Experiments I a to V d show that when barium borates and carbonate in 50% alcohol are subjected to the action of carbon dioxide in large quantities and during considerable lengths of time at temperatures from 78° C to 100° C, boric acid in some form or other is carried over with the vapors and, if they are condensed, it is present in the distillates in detectable amounts. Experiments XI, XII and XIII show that there is connection between the unlimited use of carbon dioxide and the appearance of appreciable quantities of boric acid in the distillate, because in these cases where conditions are otherwise the same, but where the carbon dioxide is restricted in amounts, the quantity of boric acid in the distillates becomes very small. It was proposed to study this matter systematically, but opportunity did not offer itself at the time these observations were made and has not presented itself since.

PART II.

The investigation in this part of the work is concerned with the action of the acid borates of barium on carbonate of barium at different temperatures. A large amount of data was collected to furnish a comparatively broad basis for any conclusions drawn: th~~is~~ese data ~~is~~ are given in the tables in this Part II.

All measuring apparatus used in this investigation was calibrated by the method of Morse and Blalock* so that measurements could be made that were accurate to one-hundredth of a cubic centimeter. Thermometers used were first examined as to the correctness of their "fixed points." Water free from carbon dioxide for use in titrations and solutions, and absolute alcohol of 99.8% by volume were prepared. Special apparatus was devised by which a standard solution of barium hydroxide could be conveniently handled, permitting the solution to be made, filtered, stored and drawn into a burette when desired without its exposure to the air at any time. The

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*American Chemical Journal XVI, 479.

basis to which all volumetric work was referred was a solution of sulphuric acid standardized by precipitating and weighing the acid from measured volumes of it as barium sulphate. In titrating, barium hydroxide solution was always run into sulphuric acid solution. Pure boric acid was prepared in two ways from boric acid gotten by decomposing borax in solution, by sulphuric acid. By the one, the crude acid after being washed well with cold water was introduced into a flask connected by a U-shaped tube (reversed) with an upright condenser and a flask. By a safety tube alcohol was introduced into the flask and distilled off. The boric acid which crystallized out from the distillate was filtered off and the alcohol returned to the flask and the whole operation repeated many times. With two such pieces of apparatus considerable boric acid was collected. Before use it was always fused to a clear glass over a blast lamp, to remove alcohol and boric ethers and carbon resulting from their decomposition when heated over an ordinary burner. The other method consisted of ten recrystallizations of the crude acid from water; the product was free from sulphuric acid and showed no trace of sodium by the flame test. It was analyzed to determine if it was the normal acid, H_3BO_3, as was supposed.

This contains 43.604% of "water of constitution." Analyses were made by heating the acid, in one case, well mixed with fine copper oxide, and in another with fine sodium carbonate in a platinum boat, proceeding much as one does in determining water in silicates by the lead oxide method. However, in each case the forward end of the tube was filled with the same substance as was in the boat with the acid, and behind the boat the tube was closed with a long roll of oxidized copper gauze. The results of the analyses were as follows:-

When heated with CuO, water found,	=	43.60%
	=	42.46 %
	=	44.76 %
When heated with Na_2CO_3, " " ,	=	43.66 %
	=	44.07 %
Average		43.73 %

Three different standard solutions of boric acid were used in the work. The first was prepared by dissolving a weighed quantity of the normal acid in absolute alcohol. The second and third were prepared from fused B_2O_3 by dissolving in one case in 95.5% alcohol and in the other, in water. That these solutions might be as reliable as possible they were prepared as follows:- An empty platinum crucible enclosed in a glass-stoppered weighing bottle was carefully weighed, ~~using~~ another weighing bottle of approximately the same size being used as a tare upon the other pan. The crucible was removed and heated over a Bunsen burner, crystallized boric acid being dropped into it in small portions until it was about half-full of a semi-vitreous mass of partially dehydrated boric acid. It was then heated over the blast lamp sixteen hours, cooled in a desiccator ~~of~~ containing sulphuric acid, transferred as quickly as possible to the weighing bottle mentioned and again the weight taken as above. The gain in weight represented the B_2O_3 in the crucible. A dry beaker of about 250 C.C. capacity was placed in an empty desiccator; to it, the crucible and boric acid wer quickly transferred, the desired solvent added, and the desiccator closed. As the solvent became saturated with the acid it was poured off into the measuring flask and a fresh portion of the solvent introduced into the beaker, and the desiccator closed. By this means it was possible

to transfer all the B_2O_3 from the crucible to the measuring flask; the desiccator prevented loss of solvent and solute by evaporation which might have been appreciable in the considerable length of time required for the solution.

In all cases where alcoholic solutions were measured, corrections for temperature were applied. The advisability of this can be shown thus: The range in temperature at which measurements were made was from +17.2° C to + 28.5° C. By Recknagel's figures for 99.3% alcohol, a rise in temperature of 11.3° C would change the volume of 1000^{cc} to that of 1011.858^{cc}, or about 1.18%. When measurements are made in glass vessels this error is diminished by .05%, leaving an error of 1.13%.

In the experiments that follow the general method of proce~~eding~~dure was to run a measured volume of barium hydroxide solution into a weighed platinum dish, and then add boric acid solution in less than equivalent quantity. The conditions during passage of carbon dioxide and evaporation are given in each experiment. Repeated heatings and weighings followed evaporation. Special treatment of the material is described wherever such was used.

Determination 1.

Volume aqueous $Ba(OH)_2$ run in dish 28.15^{cc}

Weight of BaO in dish $= .2744^{g}$

Volume alcoholic (98.8%) B_2O_3 solution run in dish 14.08^{cc}

Weight of B_2O_3 in dish $= .0983^{g}$

$.0983^{g}$ B_2O_3 is equivalent to $.2158^{g}$ BaO

Ratio B_2O_3 present to BaO is approximately 4 : 5

Concentration of mixture with respect to alcohol, 33%

Theoretical weight as $BaB_2O_4 + BaCO_3 = .3896^{g}$

The material in the dish was evaporated to dryness on a water-bath, under a stream of CO_2; this required about three hours. It was cooled in a de~~s~~sicator and weighed. Then more water was added and the dish placed in an atmosphere of CO_2 during 48 hours; evaporation to dryness, cooling and weighing followed. The rest of the treatment is sufficiently described in the table which follows.

Table of Experiments in Determination 1.

	Theoretical weight .3896 ^{g}.	Weight found in grams	Change in weight.	Error
1.	Heated on water bath	.4443		+.0547
2.	Heated on water bath	.4443	0	+.0547
3.	Heated 40 min.over 3 burners	.3859	-.0584	-.0037
4.	" " " " " "	.3770	-.0089	-.0126
5.	" 15 " " " "	.3743	-.0027	-.0153
6.	" 15 " " " "	.3728	-.0015	-.0168
7.	" 15 " " " "	.3715	-.0013	-.0181
8.	" 5 " " " "	.3703	-.0012	-.0193

Determination 2

Volume aqueous B a $(O\ H)_2$ run into dish 28.49 ^{cc}

Weight of B a O in dish = .2778 ^{g}

Volume alcoholic (99.8%) B_2O_3 solution run into dish 14.13 ^{cc}

Weight of B_2O_3 in dish = .0986 ^{g}

.0986 ^{g} B_2O_3 is equivalent to .2165 ^{g} B a O.

Ratio B_2O_3 present to B a O is approximately 4 : 5.

Concentration of mixture with respect to alcohol 33%.

The material in the dish was evaporated to dryness on a water-bath, under a stream of C O . After cooling and weighing, water was added and the treatment repeated. Other experimental details are given in the table:-

Table of Experiments in Determination 2.

	Theoretical weight .3940 g	Weight found in grams.	Change in weight. in grams	Error in grams
1.	Heated 10 min. over 1 burner	.4096		+.0156
2	Heated 40 min. over 3 burners	.3833	-.0263	-.0107
3	" 15 " " " "	.3803	-.0030	-.0137
4	" 15 " " " "	.3765	-.0038	-.0175
5	" 15 " " " "	.3758	-.0007	-.0182
6	" 15 " " " "	.3733	-.0025	-.0207

Determinations 1 and 2 show that when 33% alcohol is the menstruum in which the barium carbonate has been precipitated in the presence of barium borate, the salts obtained upon evaporation undergo losses of weight upon strong heating, similar to the losses observed by Jones. The amount of carbon dioxide in these determinations was

not carefully regulated. A remarkable tendency on the part of the material after heating to gain weight while on the balance pan was observed and regarded as significant, but its further study was delayed until later. The losses in weight are roughly proportional to the intensity and duration of the heating the mixed salts have been exposed to.

If this is a general relation, then less strong heating should cause less loss in weight; carried further back this reasoning suggests the possibility of finding a temperature so moderate that repeated heatings at that temperature would not produce repeated losses. Hence, experiments might profitably be begun at the lowest temperature consistent with the removal of whatever the aqueous or alcoholic liquid that had not been driven off during the evaporation on the water-bath.

To this end a constant temperature air-bath was constructed capable of adjustment within half a degree for several hours heating. Experiments were begun at 100° C. (In the light of later experiences it seems that very interesting data might be obtained by studies at lower temperatures, but no such experiments have been made.)

The tables of determinations 3, 4, 5, 6, and 7 record these experiments, along with some at more elevated temperatures.

Determination 3.

Volume aqueous $Ba(OH)_2$ run into dish 31.87^{cc}

Weight of BaO in dish .3144^{g}

Volume alcoholic (99.8%) boric acid solution run into dish 11.46^{cc}

Weight of B_2O_3 in dish .0802^{g}

.0802^{g} B_2O_3 is equivalent to .1760^{g} BaO.

Ratio B_2O_3 present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 26%

Theoretical weight as $BaB_2O_4 + BaCO_3 = .4343^{g}$

The preparation of the material in this case was much as in the preceding determinations; however, the dish and contents were allowed to stand in an atmosphere of carbon dioxide for one hour before evaporation, and during evaporation carbon dioxide was not allowed to run over the surface of the contents of the dish. In this determination, some attempt to study the tendency to gain weight during weighing was made, but such study furnished no data for any conclusion regarding it.

Table of Experiments in Determination 3

Theoretical weight .4343	Weight found in grams	Change in wt. in grams.	Error in grams
1 Heated on water-bath 4 hours	.5400		+.1057
2 Stood in air 1 3/4 hours	.5414	+.0014	+.1071
3 Heated on water-bath 1/2 hour	.5392	-.0022	+.1049
4 Stood in air 14 1/2 hours	.5400	+.0008	+.1057
5 Heated on water bath 1/4 hour	.5381	-.0019	+.1038
6 Stood in air 1 hour	.5396	+.0015	+.1053
7 Stood in air 6 days	.5408	+.0012	+.1065
8 Heated in air-bath at 100° for 3 1/2 hours	.5382	-.0026	+.1039
9 Stood in air 1/4 hour	.5383	+.0001	+.1040
10 Stood in air 1/2 hour	.5385	+.0002	+.1042
11 Stood in air 3/4 hour	.5389	+.0004	+.1046
12 Stood in air 1 hour	.5389	± 0	+.1046
13 Stood in air 1 1/4 hours	.5390	+.0001	+.1047
14 Stood in air 1 3/4 hours	.5390	± 0	+.1047
15 Stood in air 2 1/4 hours	.5392	+.0002	+.1049
16 Heated in air-bath at 100° for 3 1/6 hours	.5351	-.0041	+.1008
17 Stood in air 1/4 hour	.5364	+.0013	+.1021
18 Stood in air 1/2 hour	.5368	+.0004	+.1025
19 Stood in air 3/4 hour	.5368	± 0	+.10[illegible]5

Determination 3 (con.)

		Weight found in grams	Change in wt in grams	Error in grams
20	Stood in air 1 hour	.5373	+.0005	+.1030
21	Stood in air 1 1/4 hours	.5368	-.0005	+.1025
22	Stood in air 1 3/4 hours	.5374	+.0006	+.1031
23	Stood in air 2 1/4 hours	.5375	+.0001	+.1032
24	Stood in air 17 3/4 hours	.5381	+.0006	+.1038
25	Heated in air-bath at 100° for 1 hour	.5337	-.0044	+.0994
26	Stood in air 1/4 hour	.5364	+.0027	+.1021
27	Stood in air 1/2 hour	.5364	± 0	+.1021
28	Stood in air 3/4 hour	.5366	+.0002	+.1023
29	Stood in air 1 hour	.5367	+.0001	+.1024
30	Stood in air 1 1/2 hours	.5372	+.0005	+.1029
31	Heated in air-bath at 110° for 1 hour	.5325	-.0047	+.0982
32	Stood in air 1/4 hour	.5352	+.0027	+.1009
33	Stood in air 1/2 hour	.5355	+.0003	+.1012
34	Stood in air 3/4 hour	.5357	+.0002	+.1014
35	Stood in air 1 hour	.5353	-.0004	+.1010
36	Stood in air 1 1/2 hours	.5355	+.0002	+.1012
37	Heated in air-bath at 110° for 1 hour	.5311	-.0044	+.0968
38	Stood in air 1/4 hour	.5339	+.0028	+.0996
39	Stood in air 1/2 hour	.5341	+.0002	+.0998

Determination 3 (con.)

	Weight found in grams	Change in wt. in grams	Error in grams.
40 Stood in air 3/4 hour -	.5342	+.0001	+.0999
41 Heated in air-bath at 110° for 2 hours	.5317	-.0025	+.0974
42 Stood in air 1/4 hour	.5336	+.0019	+.0993
43 Stood in air 1/2 hour	.5340	+.0004	+.0997
44 Stood in air 3/4 hour	.5342	+.0002	+.0999
45 Stood in air 1 hour	.5340	-.0002	+.0997
46 Stood in air 1 1/4 hours	.5340	± 0	+.0997
47 Heated in air-bath at 110° for 4 1/4 hours	.5338	-.0002	+.0995
48 Stood in air 1/4 hour	.5343	+.0005	+.1000
49 Stood in air 1/2 hour	.5346	+.0003	+.1003
50.Stood in air 3/4 hour	.5346	± 0	+.1003

Determination 4

Volume aqueous $Ba(OH)_2$ run into dish 35.99 cc

Weight of BaO in dish .5167 g

Volume alcoholic (99.8%) boric acid solution run into dish 14.13 cc

Weight of B_2O_3 in dish .0987 g

.0987 g B_2O_3 is equivalent to .2167 g BaO

Ratio of B_2O_3 present, to BaO is approximately 2 : 5

Concentration of mixture with respect to alcohol 28%.

Theoretical weight as $BaB_2O_4 + BaCO_3$ = .7015^g

The mixture was evaporated to a small volume upon a water-bath. Then carbon dioxide was passed over its surface for one-half hour, the heating being continued. After the carbon dioxide was stopped, the evaporation was carried to dryness and the experiments described in the table follow.

Table of Experiments in Determination 4.

Theoretical weight .7015^g	Weight found in grams.	Change in wt. in grams.	Error in grams.
1 Heating on water-bath to dryness	.7257		+.024[illegible]
2 Stood in air 1 1/5 hours	.7265	+.0008	+.0250
3 Heated in air-bath at 100° for 3 1/2 hours.	.7229	-.0036	+.0214
4 Stood in air 1/4 hour	.7235	+.0006	[illegible].0220
5 Stood in air 1/2 hour	.7241	+.0006	-.0226
6 Stood in air 3/4 hour	.7251	+.0006	+.023[illegible]
7 Stood in air 1 hour	.7254	+.0003	+.02[illegible]5
8 Stood in air 1 1/4 hours	.7256	+.0002	+.0237
9 Stood in air 1 3/4 hours	.7258	± 0	+.0237
10 Stood in air 2 1/4 hours	.7[illegible]58	+.0002	+.0239
11 Heated in air-bath at 100° for 3 1/6 hours.	.7230	-.0028	+.0211

Determination 4 (cont.)	Weight found in grams	Change in wt. in grams.	Error in grams
12 Stood in air 1/4 hour	.7235	+.0005	+.0216
13 Stood in air 1/2 hour	.7237	+.0002	+.0218
14 Stood in air 3/4 hour	.7238	+.0001	+.0219
15 Stood in air 1 hour	.7239	+.0001	+.0220
16 Stood in air 1 1/4 hours	.7239	± 0	+.0220
17 Stood in air 1 3/4 hours	.7241	+.0002	+.0222
18 Heated in air-bath at 100° for 1 hour	.7217	-.0024	+.0198
19 Stood in air 1/4 hour	.7222	+.0005	+.0203
20 Stood in air 1/2 hour	.7224	+.0002	+.0205
21 Stood in air 3/4 hour	.7224	± 0	+.0205
22 Stood in air 1 hour	.7225	+.0001	+.0206
23 Stood in air 2 hours	.7227	+.0005	+.0211
24 Heated in air-bath at 110° for 1 hour	.7198	-.0029	+.0183
25 Stood in air 1/4 hour	.7210	+.0012	+.0195
26 Stood in air 1/2 hour	.7213	+.0003	+.0198
27 Stood in air 3/4 hour	.7214	+.0001	+.0199
28 Stood in air 1 hour	.7207	-.0007	+.0192
29 Stood in air 1 1/2 hours	.7215	+.0008	+.0200
30 Heated in air-bath at 110° for 1 hour	.7189	-.0026	+.0174
31 Stood in air 1/4 hour	.7214	+.0025	+.0199
32 Stood in air 1/2 hour	.7217	+.0003	+.0202
33 Stood in air 3/4 hour	.7218	+.0001	+.0203

Determination 4 (cont.)

Theoretical weight .7015g	Weight found in grams	Change in wt. in grams	Error in grams
34 Heated in air-bath at 110° for 2 hours	.7175	-.0043	+.0160
35 Stood in air 1/4 hour	.7207	+.0032	+.0192
36 Stood in air 1/2 hour	.7213	+.0006	+.0198
37 Stood in air 3/4 hour	.7215	+.0002	+.0200
38 Stood in air 1 hour	.7220	+.0005	+.0205
39 Stood in air 1 1/4 hours	.7217	-.0003	+.0202

Determination 5

Volume of aqueous $Ba(OH)_2$ put into dish 31.26^{cc}

Weight of BaO in dish .4473^{g}

Volume of alcoholic (99.8%) boric acid solution put into dish 14.32^{cc}

Weight of B_2O_3 in dish .1002^{g}

.1002^{g} B_2O_3 is equivalent to .2200^{g} BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 31%

Theoretical weight as $BaB_2O_4 + BaCO_3$ = .6127^{g}

Table of Experiments in Determination 5.

	Theoretical weight .6127 g	Weight found in grams	Change in wt. in grams	Error in grams
1	Heated in air-bath at 110° for 1 hour	.6515	0	+.0388
2	Stood in air 1/4 hour	.6515	0	+.0388
3	Stood in air 1/2 hour	.6518	+.0003	+.0391
4	Stood in air 3/4 hour	.6518	0	+.0391
5	Stood in air 1 hour	.6519	+.0001	+.0392
6	Heated in air-bath at 110° for 1 hour	.6512	-.0007	+.0385
7	Stood in air 1/4 hour	.6523	+.0011	+.0396
8	Stood in air 1/2 hour	.6524	+.0001	+.0397
9	Heated in air-bath at 110° for 2 hours	.6505	-.0019	+.0378
10	Stood in air 1/4 hour	.6516	+.0011	+.0389
11	Stood in air 2 1/4 hours	.6519	+.0003	+.0392
12	Heated in air-bath at 110° for 3 hours	.6501	-.0018	+.0374
13	Stood in air 1/4 hour	.6506	+.0005	+.0379
14	Stood in air 1/2 hour	.6506	± 0	+.0379
15	Stood in air 3/4 hour	.6507	+.0001	+.0380
16	Stood in air 1 1/4 hour	.6508	+.0001	+.0381
17	Heated in air-bath at 120° for 4 hours.	.6477	-.0031	+.0350
18	Stood in air 1/4 hour	.6483	+.0006	+.0356
19	Stood in air 1/2 hour	.6483	± 0	+.0356

Determination 5 (cont.)

		Weight found in grams	Change in wt. in grams	Error in grams
20	Stood in air 3/4 hour	.6481	-.0002	+.0354
21	Stood in air 1 1/4 hours	.6484	+.0003	+.0357
22	Heatedin air-bath at 120° for 2 1/4 hours	.6477	-.0007	+.0350
23	Stood in air 1/4 hour	.6485	+.0008	+.0358
24	Stood in air 1/2 hour	.6486	+.0001	+.0359
25	Stood in air 3/4 hour	.6486	± 0	+.0359
26	Heated in air-bath at 120° for 2 hours	.6466	-.0020	+.0339
27	Stood in air 1/4 hour	.6475	+.0009	+.0348
28	Stood in air 1/2 hour	.6475	± 0	+.0348
29	Stood in air 3/4 hour	.6475	± 0	+.0348
30	Stood in air 1 1/4 hours	.6476	+.0001	+.0349
31	Heated in air-bath at 120° for 3 1/2 hours	.6468	-.0008	+.0341
32	Stood in air 1/4 hour	.6471	+.0003	+.0344
33	Stood in air 1/2 hour	.6472	+.0001	+.0345
34	Stood in air 3/4 hours	.6472	± 0	+.0345
35	Stood in air 1 1/4 hours	.6472	± 0	+.0345
36	Heated in air-bath at 120° for 4 hours	.6458	-.0014	+.0331
37	Stood in air 1/4 hour	.6465	+.0007	+.0338
38	Stood in air 1/2 hour	.6463	-.0002	+.0336

Determination 5 (cont.)	Weight found in grams	Change in wt in grams	Error in grams
39 Stood in air 3/4 hour	.6464	+.0001	+.0337
40 Stood in air 1 1/4 hours	.6465	+.0001	+.0338
41 Heated in air-bath at 120° for 3 hours	.6469	+.0004	+.0342
42 Stood in air 1 1/4 hours	.6474	+.0005	+.0347
43 Heated in air-bath at 120° for 1 1/2 hours	.6456	-.0018	+.0329
44 Heated in air-bath at 150° for 4 1/2 hours	.6380	-.0076	+.0253
45 Stood in air 1 1/4 hours	.6382	+.0002	+.0255
46 Heated in air-bath at 150° for 7 hours	.6380	-.0002	+.0253
47 Stood in air 1 1/4 hours	.6381	+.0001	+.0254
48 Heated in air-bath at 150° for 7 hours	.6390	+.0009	+.0263
49 Heated in air-bath at 150° for 6 5/6 hours	.6374	-.0016	+.0247
50 Stood in air 1 1/4 hours	.6381	+.0007	+.0254
51 Heated in air-bath at 150° for 7 1/6 hours	.6369	-.0012	+.0242
52 Stood in air 1 1/4 hours	.6371	+.0002	+.0244
53 Heated in air-bath at 175° for 7 hours	.6324	-.0047	+.0197
54 Stood in air 1 1/4 hours	.6325	+.0001	+.0198
55 Heated in air-bath at 175° for 7 hours	.6312	-.0013	+.0185
56 Stood in air 1 1/4 hours	.6317	+.0005	+.0190
57 Heated in air-bath at 175° for 9 hours	.6303	-.0014	+.0176

Determination 5 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
58 Stood in air 1 1/4 hours	.6308	+.0005	+.0181
59 Heated in air-bath at 175° for 7 1/3 hours	.6282	-.0026	+.0155
60 Stood in air 1 1/4 hours	.6288	+.0006	+.0161
61 Heated in air-bath at 175° for 9 hours	.6285	-.0003	+.0158
62 Stood in air 1 1/4 hours	.6288	+.0003	+.0161
63 Heated in air-bath at 175° for 8 5/6 hours	.6286	-.0002	+.0159
64 Stood in air 1 1/4 hours	.6282	-.0004	+.0155
65 Heated in air-bath at 175° for 5 2/3 hours	.6285	+.0003	+.0158
66 Stood in air 1 1/4 hours	.6293	+.0008	+.0166
67 Heated in air-bath at 175° for 9 1/3 hours	.6281	-.0012	+.0154
68 Stood in air 1 1/4 hours	.6290	+.0009	+.0163
69 Heated in air-bath at 175° for 9 hours	.6286	-.0004	+.0159
70 Stood in air 1 1/4 hours	.6290	+.0004	+.0163
71 Heated to redness over open burner	.6069	-.0221	-.0058
72 Stood in air over night	.6131	+.0062	+.0004
73 Heated to redness over open burner	.6046	-.0085	-.0081
74 Stood in air 1 1/4 hours	.6078	+.0032	-.0049
75 Heated to redness over open burner	.6070	-.0008	-.0057
76 " " " " " "	.6069	-.0001	-.0058

A table of the results of determinations 3, 4, and 5 was prepared in such a way as to emphasize any relations between the temperature to which the material was heated, the length of heating, the losses in weight on heating, and the gains in weight on cooling - the rate of the latter being worked out. This table is not given as no new general relations were found by its aid.

To prevent the action of the air on the material in determinations 6 and 7, it was prepared, and heated in glass stoppered weighing bottles, these being closed during weighing.

Attempts to evaporate the material in weighing-bottles upon a water-bath resulted in losses by spattering and bumping. To prevent this, a means was devised whereby boiling would take place along the walls of the weighing-bottle and above the gelatinous precipitate of barium borate and carbonate:- A cup of copper gauze was made into which the weighing bottle to be used fit snugly. Inside the cup and between its bottom and that of the weighing-bottle, a layer of asbestos about eight millimetres thick was placed. The outer cylindrical walls of the cup were wrapped with asbestos paper, the bottom of the cup being left uncovered. By placing such an arrangement upon a heated iron plate, heat is conducted by the copper gauze from the plate to the sides of the weighing bottle inside, but not to its bottom for that is prevented by the thick layer of asbestos referred to. This proved successful in ~~avoid~~ing bumping and spattering.

Determination 6 (inweighing bottle)

Volume of aqueous $Ba(OH)_2$ run into bottle 31.[illegible]5^{cc}

Weight of BaO in bottle .6854^{g}

Volume of alcoholic (99.8%) boric acid solution run into bottle 14.44^{cc}

Weight of B_2O_3 in bottle .1015^{g}

.1015^{g} B_2O_3 is equivalent to .2227^{g} BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 3

Concentration of mixture with respect to alcohol 32%

Theoretical weight as $BaB_2O_4 + BaCO_3$ = .9196^{g}

Carbon dioxide was passed over the material until it had been evaporated to dryness, this requiring about five hours.

Table of Experiments in Determination 6.

Theoretical weight	.9196^{g}		
	Weight found in grams.	Change in wt. in grams	Error in grams
1 Heated in air-bath at 120° for 2 1/2 hours.	.9401		+.0205
2 Heated in air-bath at 120° for 1 3/4 hours	.9398	-.0003	+.0202
3 Heated in air-bath at 120° for 1 hour	.9401	+.0003	+.0205
4. Heated in air-bath at 120° for 1 hour	.9396	-.0005	+.0200

Determination 6 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
5 Heated in air-bath at 110° for 6 hours	.9417	+.0021	+.0221
6 Heated in air-bath at 110° for 6 1/3 hours	.9439	+.0022	+.0243
7 Heated in air-bath at 150° for 7 hours	.9403	-.0036	+.0207
8 Heated in air-bath at 150° for 6 hours	.9327	-.0076	+.0131
9 Heated in air-bath at 150° for 7 hours	.9288	-.0039	+.0092
10 Heated in air-bath at 150° for 8 5/6 hours	.9308	+.0020	+.0112
11 Heated in air-bath at 150° for 9 1/2 hours	-9307	-.0001	+.0111
12 Heated in air-bath at 150° for 7 1/2 hours	.9292	-.0015	+.0096
13 Heated in air-bath at 150° for 9 1/2 hours	.9261	-.0031	+.0065
14 Heated in air-bath at 150° for 8 5/6 hours	.9263	+.0002	+.0067
15 Heated in air-bath at 150° for 5 2/3 hours	.9307	+.0044	+.0111
16 Heated in air-bath at 150° for 9 1/3 hours	.9292	-.0015	+.0096
17 Heated in air-bath at 150° for 9 1/2	.9306	+.0014	+.0110
18 Heated in air-bath at 175° for 9 hours	.9256	-.0050	+.0060
19 Heated in air-bath at 175° for 23 hours	.9211	-.0045	+.0015

Determination 6 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
20 Heated in air-bath at 175° for 3 1/2 hours	.9230	+.0019	+.0034
21 Heated in air-bath at 175° for 9 1/2 hours	.9231	+.0001	+.0035

Determination 7 .

Volume of aqueous $Ba(OH)_2$ run into bottle 31.25^{cc}

Weight of BaO in bottle .6868^{g}

Volume of alcoholic (99.8%) boric acid solution run into bottle 14.38^{cc}

Weight of B_2O_3 in bottle .1010^{g}

.1010^{g} B_2O_3 is equivalent to .2218^{g} BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 3

Concentration of mixture with respect to alcohol 32%

Theoretical weight for $BaB_2O_4 + BaCO_3$ = .8213^{g}

The evaporation and passage of carbon dioxide was conducted as in determination 6.

Table of Experiments in Determination 7

	Weight found in grams	Change in wt. in grams	Error in grams
Theoretical weight	.9213g		
1 Heated in air-bath at 120° for 2 1/2 hours	.9385		+.0172
2 Heated in air-bath at 120° for 1 3/4 hours	.9323	-.0062	+.0110
3 Heated in air-bath at 120° for 1 hours	.9332	+.0009	+.0119
4 Heated in air-bath at 120° for 1 hour	.9331	-.0001	+.0018
5 Heated in air-bath at 110° for 6 hours	.9375	+.0044	+.0162
6 Heated in air bath at 110° for 6 1/3 hours	.9350	-.0025	+.0137
7 Heated in air-bath at 150° for 7 hours	.9344	-.0006	+.0131
8 Heated in air-bath at 150° for 6 hours	.9232	-.0112	+.0019
9 Heated in air-bath at 150° for 7 hours	.9233	+.0001	+.0020
10 Heated in air-bath at 150° for 8 5/6 hours	.9260	+.0027	+.0047
11 Heated in air-bath at 150° for 9 1/2 hours	.9264	+.0004	+.0051
12 Heated in air-bath at 150° for 7 1/2 hours	.9255	-.0009	+.0042
13 Heated in air-bath at 150° for 9 1/2 hours	.9259	+.0004	+.0046
14 Heated in air-bath at 150° for 8 5/6 hours	.9223	-.0036	+.0010

Determination 7 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
15 Heated in air-bath at 150° for 5 2/3 hours	.9258	+.0035	+.0045
16 Heated in air-bath at 150° for 9 1/3 hours	.9253	-.0005	+.0040
17 Heated in air-bath at 150° for 9½ hours	.9251	-.0002	-.0038
18 Heated in air-bath at 175° for 9 hours	.9205	-.0046	-.0008
19 Heated in air-bath at 175° for 23 hours	.9183	-.0022	-.0030
20 Heated in air-bath at 175° for 3 1/2 hours	.9216	+.0033	+.0003
21 Heated in air-bath at 175° for 9 1/2 hours	.9196	-.0020	-.0017

Determinations 6 and 7 show that there is no connection between the losses in weight on heating and the intermediate contact with the air during weighing.

Determinations 3 to 7 show that at lower temperatures there is small hope of obtaining constant weight,- at least between 100° C and 175° C.

In those experiments where the heating had been sufficiently intense to carry the weight of the mixed salts below the theoretical for a mixture of BaB_2O_4 and $BaCO_3$ it was

noticed that the tendency to gain weight, already referred to, seemed to be at a maximum. More data on this point ~~was~~ were desired, and ha~~s~~ve been collected in many of the determinations that follow.

Determination 8.

Volume of aqueous $Ba(OH)_2$ put into dish 20.39^{cc}

Weight of BaO in dish .5611^{g}

Volume of alcoholic (95.5%) boric acid solution run into dish 16.90^{cc}

Weight of B_2O_3 in dish .1259^{g}

.1259^{g} B_2O_3 is equivalent to .2764^{g} BaO

Ratio BO present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 43%

Theoretical weight for a mixture of BaB_2O_4 and $BaCO_3$ .7687^{g}

The contents of the dish were evaporated to a small volume and, while still heated on a water-bath, carbon dioxide was passed over the surface of the liquid for fifteen minutes under constant stirring with a platinum rod. The evaporation to dryness was completed on an iron plate. In experiments 10 and 11 (see table) the dried material was moistened, a drop of phenol-phthalein added and carbon dioxide passed over it to neutral reaction; this was while the material was kept hot on a water-bath.

Table of Experiments in Determination 8.

Theoretical weight .7687^{g}

	Weight found in grams	Change in wt. in grams	Error in grams
Heated to redness over open burner	.7513		-.0174
" " " " " "	.7500	-.0013	-.0187
Stood in air 3 hours	.7559	+ 0059	-.0128
Stood in air 15 hours	.7663	+.0104	-.0024
Stood in air 48 hours.	.7744	+.0081	+.0057
Stood in air 50 1/2 hours	.7741	-.0003	+.0054
Heated to redness over open burner	.7536	-.0205	-.0151
Heated to redness over open burner	.7560	+.0024	-.0127
Heated to redness over open burner	.7542	-.0018	-.0145
Moistened, saturated with CO_2 heated over burner	.7667	+.0125	-.0020
Moistened, saturated with CO_2 heated over burner	.7704	+.0037	+.0017

The tendency to gain weight on the part of the mixed salts during weighing has been remarked - and it has been stated that this is very pronounced in all cases where the preceding heating has been sufficient to carry the weight of the material below the theoretical for a mixture of [illegible] a B_2O_4

and $BaCO_3$. Determination 8 confirmed this; also it showed that by the action of water and carbon dioxide, material that has been quite far below the theoretical weight takes on weight enough to run above it.

Determination 9.

Volume of aqueous $Ba(OH)_2$ run into dish		10.84^{cc}
Weight of BaO in dish	$.2985^{g}$	
Volume of alcoholic (95.5%) boric acid solution run into dish		8.97^{cc}
Weight of B_2O_3 in dish	$.0668^{g}$	

$.0686^{g}$ B_2O_3 is equivalent to $.1478^{g}$ BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 43%

Theoretical weight for a mixture of BaB_2O_4 $BaCO_3$ $.4088^{g}$

Evaporated to small volume on water-bath, passed carbon dioxide over the surface for fifteen minutes while still being heated and constantly stirred. Then completed evaporation to dryness. In experiments 8, 13, 14 and 42 phenol-phthalein was used as indiactor in the passage of carbon dioxide.

Table of Experiments in Determination 9

Theoretical weight .4088 g

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated to redness over burner	.4029		-.0059
2 " " " " "	.4008	-.0021	-.0080
3 Stood in air 3 hours	.4037	+.0029	-.0051
4 Stood in air over night, 17 hrs.	.4082	+.0045	-.0006
5 Stood in air 65 hours	.4111	+.0029	+.0023
6 Stood in air 67 1/2 hours	.4120	+.0009	+.0032
7 Stood in air 71 1/2 hours	.4109	-.0011	+.0021
8 Moistened, saturated with CO_2, heated to redness	.4195	+.0086	+.0107
9 Heated to redness over open burner	.4156	-.0039	+.0068
10 Heated to redness over open burner	.4119	-.0037	+.0031
11 Heated to redness over open burner	.4104	-.0015	+.0016
12 Heated to redness over open burner	.4094	-.0010	+.0006
13 Moistened, saturated with CO_2, heated to redness	.4178	+.0084	+.0090
14 Moistened, saturated with CO_2, heated to redness	.4128	-.0050	+.0040
15 Heated to redness over open burner	.4101	-.0027	+.0013
16 Heated longer and to higher temperature	.4037	-.0064	-.0051
17 Heated longer and to higher temperature	.4020	-.0017	-.0068

Determination 9 (cont.)

	Weight found in grams	Change in weight in gr.	Error in grams
18 Heated longer and to higher temperature	.4016	-.0004	-.0072
19 Stood in air 10 minutes	.4026	+.0010	-.0062
20 Stood in air 20 minutes	.4036	+.0010	-.0052
21 Stood in air 30 minutes	.4046	+.0010	-.0042
22 Stood in air 40 minutes	.4053	+.0007	-.0035
23 Stood in air 50 minutes	.4059	+.0006	-.0029
24 Stood in air 60 minutes	.4062	+.0003	-.0026
25 Stood in air 70 minutes	.4066	+.0004	-.0022
26 Stood in air 90 minutes	.4075	+.0009	-.0013
27 Stood in air 110 minutes	.4080	+.0005	-.0008
28 Stood in air 175 minutes	.4090	+.0010	+.0002
29 Stood in air 24 hours	.4104	+.0014	+.0016
30 Stood of $CaCl_2$ for 2 hours	.4098	-.0006	+.0010
31 Stood " " " 7 "	.4097	-.0001	+.0009
32 " " " " 9 "	.4095	-.0002	+.0007
33 " " " " 24 "	.4094	-.0001	+.0006
34 Heated to redness over open burner	.4049	-.0045	-.0009
35 Heated to redness over open burner	.4035	-.0014	-.0053
36 Heated to redness over open burner	.3973	-.0062	-.0115
37 Heated to redness over open burner	.3975	+ 0002	-.0113

Determination 9 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
38 Heated to redness over open burner	.3971	-.0004	-.0117
39 Heated to redness over open burner	.3972	+.0001	-.0116
40 Heated to redness over open burner	.3973	+.0001	-.0115
41 Heated to redness over open burner	.3962	-.0011	-.0126
42 Moistened, saturated with CO_2, evaporated and heated over open burner	.4111	+.0149	+.0023
43 Heated to redness over open burner	.4086	-.0025	-.0002
44 Heated to redness over open burner	.4060	-.0026	-.0028
45 Heated to redness over open burner	.4054	-.0006	-.0034
46 Heated to redness over open burner	.4023	-.0031	-.0065
47 Heated to redness over open burner	.4016	-.0007	-.0072
48 Heated to redness over open burner	.4002	-.0014	-.0086
49 Heated to redness over open burner	.3995	-.0007	-.0093
50 Stood in air 15 hours	.4090	+.0095	+.0002
51 Stood in air 171/2 hours	.4091	+.0001	+.0003
52 Stood in air 19 1/2 hours	.4093	+.0002	+.0005
53 Stood in air 22 hours	.4096	+.0003	+.0008
54 Stood in air 39 hours	.4104	+.0008	+.0016
55 Stood over $CaCl_2$ for 3 hours	.4094	-.0010	+.0006
56 Stood over $CaCl_2$ for 6 1/2 hours	.4095	+.0001	+.0007

Determination 10

Volume of aqueous $Ba(OH)_2$ run into dish 10.91^{cc}

Weight of BaO in dish .3038

Volume of alcoholic (95.5%) boric acid solution 8.95^{cc}

Weight of B_2O_3 in dish $.0669^g$

$.0669^g$ B_2O_3 is equivalent to $.1468^g$ BaO

Ratio B_2O_3 present, to BaO 1 : 2

Concentration of mixture with respect to alcohol 43%

Theoretical weight for a mixture of $BaB_2O_4 + BaCO_3$ $.4157^g$

Treatment same as in Determination 9.

Table of Experiments in Determination 10.

Theoretical weight $.4157^g$

	Weight found in grams	Change in weight in grams	Error in grams
1 Heated to redness over burner	.4042		-.0115
2 Stood in air 2 hours	.4040	-.0002	-.0117
3 Stood in air 17 hours	.4099	+.0059	-.0058
4 Stood in air 65 hours	.4177	+.0078	+.0020
5 Stood in air 67 1/2 hours	.4179	+.0002	+.0022
6 Stood in air 71 1/2 hours	.4177	-.0002	+.0020
7 Moistened, saturated with CO_2 evap., heated to redness over burner	.4335	+.0158	+.0178

Determination 10 (cont.)

		Weight found in grams	Change in wt. in grams	Error in grams
8	Heated to redness over burner	.4291	-.0044	+.0134
9	Heated to redness over open burner	.4251	-.0040	+.0094
10	Heated to redness over open burner	.4255	+.0004	+.0098
11	Heated to redness over open burner	.4242	-.0013	+.0085
12	Moistened, saturated with CO_2 evaporated and heated to redness	.4256	+.0014	+.0099
13	"	.4273	+.0017	+.0116
14	Heated to redness over open burner	.4221	-.0052	+.0064
15	Heated longer and to higher temperature	.4077	-.0144	-.0080
16	Heated to redness over open burner	.4065	-.0012	-.0092
17	Heated to redness over open burner	.4064	-.0001	-.0093
18	Stood in air 10 minutes	.4076	+.0012	-.0081
19	" " " 20 "	.4085	+.0009	-.0072
20	" " " 30 "	.4090	+.0005	-.0067
21	" " " 40 "	.4096	+.0006	-.0061
22	" " " 50 "	.4101	+.0005	-.0055
23	" " " 60 "	.4105	+.0004	-.0051
24	" " " 70 "	.4110	+.0005	-.0046
25	" " " 90 "	.4117	+.0007	-.0039
26	" " " 110 "	.4122	+.0005	-.0034

(Determination 10 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
27 Stood in air 175 minutes	.4137	+.0015	-.0019
28 Stood in air 24 hours	.4193	+.0056	+.0030
29 Stood over H_2SO_4 for 2 hrs.	.4172	-.0021	+.0015
30 Stood over H_2SO_4 for 7 hrs.	.4177	+.0005	+.0020
31 " " " 9	.4158	-.0019	+.0001
32 " " " 24 "	.4159	+.0001	+.0002
33 Heated to redness over open burner	.4092	-.0067	-.0065
34 Heated to redness over open burner	.4073	-.0019	-.0084
35 Heated to redness over open burner	.4053	-.0020	-.0104
36 Heated to redness over open burner	.4049	-.0004	-.0108
37 Heated to redness over open burner	.4043	-.0006	-.0114
38 Heated to redness over open burner	.4042	-.0001	-.0115
39 Heated to redness over open burner	.4038	-.0004	-.0119
40 Heated to redness over open burner	.4033	-.0005	-.0124
41 Moistened, saturated with CO_2 evaporated and heated to redness over open burner	.4244	+.0211	+.0087
42 Heated to redness over open burner	.4215	-.0029	+.0058
43 Heated to redness over open burner	.4185	-.0030	+.0028

Determination 10 (cont.)

	Weight found in grams	Change in weight in grams	Error in grams
44 Heated to redness over open burner	.4144	-.0041	-.0013
45 Heated to redness over open burner	.4092	-.0052	-.0065
46 Heated to redness over open burner	.4083	-.0009	-.0074
47 Heated to redness over open burner	.4070	-.0013	-.0087
48 Heated to redness over open burner	.4034	-.0036	-.0123
49 Stood in atmosphere of CO_2 saturated with H_2O, 15 hrs.	.4688	+.0654	.0531
50 Heated to redness over open burner	.4102	-.0586	-.0055
51 Stood in air 2 3/4 hours	.4124	+.0022	-.0033
52 Stood in air 20 hours	.4189	+.0065	+.0032
53 Stood over $CaCl_2$ 2 hours	.4173	-.0016	+.0016
54 Stood over $CaCl_2$, 5 1/2 hrs.	.4170	-.0003	+.0013
55 Stood over H_2SO_4 6 1/2 hrs.	.4164	-.0006	+.0007

Determination 11

Volume of aqueous $Ba(OH)_2$ run into dish 12.29^{cc}

Weight of BaO in dish .3448^{g}

Volume of alcoholic (95.5%) boric acid solution run into dish 13.39^{cc}

Weight of B_2O_3 in dish .0999^{g}

.0999 B_2O_3 is equivalent to .2192^g B a O

Ratio of B_2O_3 present, to B a O is approximately 2 : 3

Concentration of mixture with respect to alcohol 46%

Theoretical weight for a mixture of $BaB_2O_4 + BaCO_3$ .4807^g

A drop of phenol-phthalein was added and during evaporation upon a water-bath carbon dioxide was passed to neutral re-action.

Table of Experiments in Determination 11.

Theoretical weight .4807^g

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated to incipient redness	.4854		+.0047
2 " " " "	.4803	-.0051	-.0004
3 " " " "	.4751	-.0052	-.0056
4 " " " "	.4749	-.0002	-.0058
5 " " " "	.4744	-.0005	-.0063
6 " " " "	.4727	-.0017	-.0080
7 Moistened, saturated with CO_2 evaporated and heated to incipient redness	.4961	+.0234	+.0154
8 Heated to redness over burner	.4918	-.0043	+.0111

Determination 11 (cont.)

		Weight found in grams	Change in wt. in grams	Error in grams
9	Heated to redness over burner	.4904	-.0014	+.00[illegible]7
10	Heated to redness over burner	.4870	-.0034	+.0063
11	" " " "	.4829	-.0041	+.0022
12	" " " "	.4807	-.0022	$\pm$ 0
13	" " " "	.4790	-.0017	-.0017
14	" " " "	.4763	-.0027	-.0044
15	Stood in air for 4 hours	.4793	+.0030	-.0014
16	Stood in air for 21 1/2 hours	.4827	+.0034	+.0020
17	" " " " 24 "	.4829	+.0002	+.0022
18	Stood over $CaCl_2$ for 4 5/6 hrs.	.4824	-.0005	+.0017
19	" " " " 12 hrs.	.4819	-.0005	+.0012
20	" " H_2SO_4 " 12 hrs.	.4816	-.0003	+.0009

Determination 12.

Volume of aqueous $Ba(OH)_2$ run into dish 12.19^{cc}

Weight of BaO in dish .3417^{g}

Volume of alcoholic (95.5%) boric acid solution 13.38^{cc}

Weight of B_2O_3 in dish .1000^{g}

.1000^{g} B_2O_3 is equivalent to .2195^{g} BaO

Ratio B_2O_3 present, to BaO is approximately 2 : 3

Concentration of mixture with respect to alcohol .5%

Theoretical weight for a mixture of BaB_2O_4 and $BaCO_3$ .4768[g]

Carbon dioxide was conducted through the liquid by means of a platinum tube that was weighed with the dish; the operation, which was carried on at room temperature was regulated by phenol-phthalein indicator; after this, the material was evaporated to dryness on a water bath.

Table of Experiments in Determination 12.

Theoretical weight .4768[g]

		Weight found in grams	Change in wt. in grams	Error in grams
1	Heated to incipient redness	.5002		+.0234
2	Heated to incipient redness	.4900	-.0102	+.0132
3	" " " "	.4867	-.0033	+.0099
4	" " " "	.4858	-.0009	+.0090
5	" " " "	.4811	-.0047	+.0043
6	" " " "	.4807	-.0004	+.0039
7	" " " "	.4794	-.0013	+.0026
8	" " " "	.4778	-.0016	+.0010
9	" " " "	.4770	-.0008	+.0002
10	" " " "	.4763	-.0007	-.0005
11	" " " "	.4764	+.0001	-.0004
12	" " " "	.4765	+.0001	-.0003

Determination 12 (cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
13 Stood in air 16 hours	.4777	+.0012	+.0009
14 " " " 18 "	.4774	-.0003	+.0006
15 " " " 22 "	.4780	+.0006	+.0012
16 Stood over $CaCl_2$ 16 hours	.4782	+.0002	+.0014
17 " " H_2SO_4 24 hours	.4778	-.0004	+.0010

Determination 13

Volume of aqueous $Ba(OH)_2$ put into dish 14.59 cc

Weight of BaO in dish .3882 g

Volume of alcoholic (95.5%) boric acid solution put into dish 11.97 cc

Weight of B_2O_3 in dish .0888 g

.0888 g B_2O_3 is equivalent to .1950 g BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 43%

Theoretical weight for a mixture of $BaB_2O_4 + BaCO_3$ = .53[illegible]4 g

A drop of phenol-phthalein indicator was added, carbon dioxide passed over material in cold with frequent stirring to neutral reaction; evaporated to dryness and heated.

Table of Experiments in Determination 13.

Theoretical weight .5324 g

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated to redness	.5288		-.0036
2 Heated again and stood in air 2 hours	.5300	+.0012	-.0024
3 Stood in air 24 hours	.5317	+.0017	-.0007
4 Moistened, saturated with CO_2 evaporated, heated to redness	.5375	+.0058	+.0051
5 Heated to redness	.5350	-.0025	+.0026
6 " " "	.5332	-.0018	+.0008
7 " " "	.5318	-.0014	-.0006
8 Stood in air 29 hours	.5407	+.0089	+.0083
9 Stood over H_2SO_4 1 hour	.5398	-.0009	+.0074
10 Heated to redness four minutes and stood in air 21 hours	.5368	-.0030	+.0044
11 Stood over H_2SO_4 for 24 hrs.	.5327	-.0041	+.0003
12 Stood in air for 24 hours	.5412	+.0085	+.0082

Determination 14.

Volume of aqueous $Ba(OH)_2$ put into dish 14.54 cc

Weight of BaO in dish .3879 g

Volume of alcoholic (95.5%) boric acid solution put into dish 5.96 cc

Weight of B_2O_3 in dish .0441^g

.0441^g B_2O_3 is equivalent to .0968^g B a O

Ratio B_2O_3 present, to B a O is approximately 1 : 4

Concentration of mixture with respect to alcohol 27%

Theoretical weight for a mixture of B a B_2O_4 + B a C O_3 .5154^g

A drop of phenol-phthalein was added and carbon dioxide passed over the mixture in the cold, to neutral reaction; evaporation to dryness on water-bath followed, and then the heating, etc.

Table of Experiments in Determination 14.

Theoretical weight .5154^g

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated to redness	.5130		-.0024
2 Stood in air 8 hours	.5280	+.0150	+.0126
3 Stood in air 72 hours	.5300	+.0020	+.0146
4 Stood over H_2SO_4 8 1/2 hours	.5287	-.0013	+.0133
5 " " " 26 "	.5283	-.0004	+.0129
6 Heated to redness	.5168	-.0115	+.0114
7 Stood in air 19 hours	.5255	+.0087	+.0101
8 Stood over H_2SO_4 23 hours	.5250	-.0005	+.0096
9 Heated 4 minutes to redness	.5048	-.0202	-.0106
10 Stood in air 25 1/2 hours	.5310	+.0262	+.0156

Determination 15

Volume of aqueous $Ba(OH)_2$ run into dish 7.26^{cc}

Weight of BaO in dish .1938^{g}

Volume of alcoholic (95.5%) boric acid solution run into dish 3.03^{cc}

Weight of B_2O_3 in dish .0224

.0224^{g} B_2O_3 is equivalent to .0491 BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 4

Concentration of mixture with respect to alcohol 28%

A drop of phenolphthalein indicator was added and carbon dioxide passed over the mixture at the room temperature, to neutral reaction; evaporation to dryness upon the water-bath followed and then heatings, etc.

Table of Experiments in Determination 15.

Theoretical weight .2576^{g}

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated to redness	.2557		-.0019
2 " " "	.2553	-.0004	-.0023
3 Stood in air 1/2 hours	.2652	+.0099	+.0076
4 " " " 26 "	.2665	+.0013	+.0089
5 " over H_2SO_4 22 hours	.2645	-.0020	+.0069
6 Heated 4 min. to redness and stood in air 24 hours	.2648	-.0003	+.0072
7 Stood over H_2SO_4 25 hours	.2588	-.0060	+.0012

The heatings in all the experiments so far described at temperatures above 175° have been accomplished by bunsen burners. It is very difficult to say what the temperatures to which the material was exposed in such experiments, were. With the object of obtaining high temperatures which would remain fairly constant and could be measured, a special air-bath to be heated by three large burners was devised and set up. Glass thermometers, containing carbon dioxide under twenty atmospheres pressure above the mercury column, were used; 520° C was their maximum registering limit. The determinations that follow involve the use of this hot-air bath. It was found later that yet higher temperatures than could be attained in this apparatus had to be used; at such temperatures some very interesting changes occur, but this part of the study could not be carried out except over the open bunsen burner at an indefinite, though sufficiently high, temperature.

Determination 16.

Volume of aqueous $Ba(OH)_2$ run into dish		14.93^{cc}
Weight of BaO in dish	$.3810^{g}$	
Volume of alcoholic (95.5%) boric acid solution run into dish		12.36^{cc}
Weight of B_2O_3 in dish	$.0920^{g}$	

.0920^{g} B_2O_3 is equivalent to .2019^{g} BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 2

Concentration of mixture with respect to alcohol 43%.

Theoretical weight for a mixture of BaB_2O_4 and $BaCO_3$ .5244^{g}

A drop of phenol-phthalein indicator was added and carbon dioxide passed to neutral reaction and some few minutes longer. This operation was carried on at the temperature of the room. Evaporation to dryness on a water-bath followed, and then heatings, etc.

Table of Experiments in Determination 16.

Theoretical Weight .5244

	Weight found in grams	Change in weight in grams	Error in grams
1 Heated at 450°-470° for 5 hrs.	.5576		+.0332
2 Stood 1 1/4 hours ~~on balance~~ in air	.5601	+.0025	+.0357
3 Heated above 510° for 5 hours	.5548	-.0053	+.0304
4 " " " " 2 "	.5508	-.0040	+.0264
5 " " " " 3 "	.5468	-.0040	+.0224
6 " " " " 9 "	.5322	-.0146	+.0078
7 " " " " 6 "	.5224	-.0098	-.0020
8 Stood in air 3/4 hour	.5238	+.0014	-.0006
9 " " " 2 1/4 hours	.5270	+.0032	+.0026
10 " " " 24 hours	.5282	+.0012	+.0038

Determination 16 (cont.)

		Weight found in grams	Change in wt. in grams	Error in grams
11	Stood over H_2SO_4 48 hours	.5276	-.0006	+.0032
12	Heated above 510° for 7 hours	.5218	-.0058	-.0026
13	Stood in air 3/4 hours	.5225	+.0007	-.0019
14	" " " 4 "	.5259	+.0034	+.0015
15	" " " 8 "	.5264	+.0005	+.0020
16	" " " 24 "	.5268	+.0004	+.0024
17	Stood over H_2SO_4 for 3 hours	.5266	-.0002	+.0022
18	" " " " 9 "	.5264	-.0002	+.0020
19	" " " " 24 "	.5264	$\pm$ 0	-.0020
20	Heated at 450°-470° for 9 1/2 hrs	.5250	-.0014	+.0006
21	Stood in air for 24 hours	.5261	+.0011	+.0017
22	Stood over H_2SO_4 for 48 hrs.	.5260	-.0001	+.0016
23	Heated to redness over open burner	.5158	-.0102	-.0086
24	Stood over KOH solution 6 hrs.	.5368	+.0210	+.0124
25	Stood over H_2SO_4 for 66 1/2 hrs.	.5258	-.0110	+.0014
26	Stood over H_2SO_4 for 68 1/2 hrs.	.5257	-.0001	+.0013
27	Heated at 450°-470° for [illegible] hrs.	.5236	-.0021	-.0008
28	Stood in air 1 hour	.5240	+.0004	-.0004
29	Heated at 460°-470° for 4 hrs.	.5248	+.0008	+.0004
30	Stood in air 1 hour	.5248	$\pm$ 0	+.0004
31	Heated about 510° for 9 hrs.	.5273	+.0025	+.0029
32	Stood in air 1/4 hour	.5275	+.0002	+.0031

(Determination 16 cont.)

	Weight found in grams	Change in wt. in grams	Error in grams
33 Heated to redness over open burner	.5218	-.0057	-.0026
34 Heated at 450°-470° for 2 hrs.	.5252	+.0034	+.0008
35 " " " " " 1 hr.	.5254	+.0002	+.0010
36 " " " " " 1 hr.	.5255	+.0001	+.0011
37 Heated to redness over open burner	.5190	-.0065	-.0054
38 Heated at 450°-460° for 1 hr.	.5222	+.0032	-.0022
39 " " " " for 1 1/2 hr.	.5236	+.0014	-.0008
40 Heated at 450°-460°, 1hr, and let cool in air	.5243	+.0007	-.0001
41 " "450°-460°, 1 hr., and let cool in air	.5245	+.0002	+.0001
42 " " 450-460°, 1 hr., and let cool in air	.5246	+.0001	+.0002
43 Heated at 450°-460°, 1 hr., and let cool in air	.5248	+.0002	+.0004
44 Heated at 450°-460°, 1 hr., and let cool in air	.5250	+.0002	+.0006
45 Heated at 450°-460°, 1 hr., and let cool in air	.5251	+.0001	+.0007

Determination 17.

Volume of aqueous $Ba(OH)$ run into dish 7.45 cc

Weight of BaO in dish .1866 g

Volume of alcoholic (95.5) boric acid solution run into dish — 2.[illegible] cc

Weight of B_2O_3 in dish .0221

.0221 B_2O_3 is equivalent to .0485 B a 0

Ratio B_2O_3 present, to B a O is approximately 1 : 4

Concentration of mixture with respect to alcohol 27

Theoretical weight for a mixture of B a B_2O_4 and B a CO_3 .2483

Treatment with carbon dioxide, etc., same as in determination 16.

Table of Experiments in Determination 17.

Theoretical weight .2483

		Weight found in grams	Change in wt. in grams	Error in grams
1	Heated at 480° for 1 1/2 hours	.2556		+.0073
2	Stood in air for 48 hours	.2563	+.0007	+.0080
3	Heated above 510° for 6 hours	.2457	-.0106	-.0026
4	Stood in air for 48 hours	.2488	+.0031	+.0005
5	Stood over H_2SO_4 for 24 hrs.	.2480	-.0008	-.0003
6	Heated above 510° for 8 1/2 hrs.	.2416	-.0064	-.00[illegible]7
7	Stood in air for 3/4hour	.2444	+.0028	-.0039
8	Stood in air for 2 1/2 hrs.	.2484	+.0040	+.0001
9	Stood in air for 9 hours	.2525	+.0041	+.0042
10	Stood in air for 24 hours	.2537	+.0012	+.0054

Determination 17 (cont.)

	Weight found in grams	Change in wt. found grams	Error in grams
11 Stood over $H_2S\ O_4$ for 9 1/2 hours	.2526	-.0011	+.0043
12 Stood in air for 14 hours	.2539	.0013	.0056
13 Heated at 450°-470° for 8 hrs.	.2485	-.0054	+.0002
14 Stood in air for 48 hours	.2491	+.0006	+.0008

Determination 18.

Volume of aqueous $B\ a\ (O\ H)_2$ run into dish 15.00 cc

Weight of B a O in dish .3790 g

Volume of aqueous boric acid solution run into dish 14.24 cc

Weight of B_2O_3 in dish .0905 g

.0905 g B_2O_3 is equivalent to .1986 g B a O.

Ratio B_2O_3 present, to B a O is approximately 1 : 2

Theoretical weight for a mixture of $Ba\ B_2O_4 + B\ a\ C\ O_3$ = .5212 g

Treatment with carbon dioxide, etc., same as in determination 16.

Table of Experiments in Determination 18.

Theoretical weight .5212 g

		Weight found in grams	Change in wt. in grams	Errors in grams
1	Heated at 490°-510° for 9 1/2 hrs.	.5416		+.0204
2	Stood over H_2SO_4 for 24 hours	.5418	+.0002	+.0206
3	Heated at 490°-510° for 9 hrs.	.5406	-.0012	+.0194
4	Heated at 460°-470° for 9 hrs.	.5392	-.0014	+.0180
5	Heated to redness over open burner	.5188	-.0204	-.0024
6	Stood over K O H solution for 6 hours	.5451	+.0263	+.0239
7	Stood over H_2SO_4 for 66 1/2 hrs.	.5316	-.0135	+.0104
8	Stood over H_2SO_4 for 68 1/2 hrs.	.5316	± 0	+.0104
9	Stood over K O H solution 6 1/2 hours	.5536	+.0220	+.0324
10	Stood over K O H solution 21-1/2 hours	.5546	+.0010	+.0334
11	Stood over H_2SO_4 for 48 hrs.	.5372	-.0174	+.0160
12	Heated at 450°-460° for 1 1/2 hours	.5232	-.0140	+.0020
13	Heated to redness over open burner	.5162	-.0070	-.0050
14	Heated at 440°-460° for 1 hr.	.5204	+.0042	-.0008
15	Heated at 440°-460° for 1 hr.	.5216	+.0012	+.0004
16	Heated at 440°-460° for 1 hr.	.5219	+.0003	+.0007
17	" " " " " " "	.5224	+.0005	+.0012
18	" " " " " " "	.5252	+.0028	+.0040
19	" to redness over open burner	.5199	-.0053	-.0013
20	Heated at 440°-460° for 1 hr.	.5230	+.0031	+.0018

Determination 19.

Volume of aqueous $Ba(OH)_2$ run into dish 7.00 cc

Weight of BaO in dish .1947 g

Volume of aqueous boric acid solution run into dish 2.54 cc

Weight of B_2O_3 in dish .0161 g

.0161 g B_2O_3 is equivalent to .0354 g BaO

Ratio B_2O_3 present, to BaO is approximately 1 : 6

Theoretical weight for a mixture of BaB_2O_4 and $BaCO_3$ .2565 g

The treatment with carbon dioxide, etc was same as in determination 16.

Table of Experiments in Determination 19.

Theoretical weight .2565 g

	Weight found in grams	Change in wt. in grams	Error in grams
1 Heated above 510° for 3 hours	.2577		+.0012
2 Heated to redness over open burner	.2548	-.0029	-.0017
3 Heated at 450°-470° for 2 hrs.	.2557	+.0009	-.0008
4 " " " " " " "	.2557	± 0	-.0008
5 Stood over KOH solution 1 1/4 hrs.	.2573	+.0016	+.0008
6 Stood over H_2SO_4 for 60 hrs.	.2565	-.0008	± 0
7 Heated at 450°-470° for 1 1/2hrs.	.2560	-.0005	-.0005
8 Heated at 450°-470° for 1 hr. and cooled in air	.2563	+.0003	-.0002

Conclusions of Part II:-

The facts brought out are these:-

(1) The behavior of the mixed salts in hand is similar whether the ratio of B_2O_3 to BaO be 1 : 2, 1 : 3, 1 : 4, 1 : 6

2 : 3, 2 : 5

4 : 5

and whatever the liquid in which they are precipitated.

(2) When CO_2 is passed into a mixture of barium borate and hydroxide to neutral reaction with phenol-phthalein, after evaporation, the weight is always greater than the theoretical for a corresponding mixture of BaB_2O_4 and $BaCO_3$. After heatings have been made and losses in weight have occurred, the addition of water and CO_2, produces likewise the same effect, giving excessive weight. IX. 8, 13, 14, 42.

X. 7, 12, 13, 41, 49.

XI. 1, 7;

XII 1;

XIII 4.

(3) When such a mixture possessing excessive weight as compared with the theoretical for $BaB_2O_4 + BaCO_3$ is subjected to repeated heatings at the same or gradually increasing temperatures, losses in weight occur depending upon the length and degree of the heating

III; IV; V; VI; VII at lower temperatures

I; II; IX, 9 - 12, 15, 18, 43 - 49;

X. 33- 40, 42 - 48; XI. 1 - 6, 8 - 14.

XII, 1 - 11; XIII, 4- 7; XVI, 3 - 7.

(4) Along with the losses in weight and roughly inversely proportional to them is developed a tendency, in each case, to take on weight upon exposure to the air.

III; IV; V

IX, 3 - 7, 19 - 29, 50-54; X. 2-6,18-28, 50-52;

XI, 15-17; XII, 13-15; XIII, 3, 8; XIV,2, 3, 8;

XV. 3 and 4; XVI, 8-10, 13-16,21; XVII,2,7,-10.

(5) If the material before exposure to the air has not been heated to redness, at least, and for a considerable length of time, then it may ~~take on~~ increase in weight when exposed over and above that required for a mixture of $BaB_2O_4 + BaCO_3$; and this excess cannot be removed by des~~s~~ication.

XIV. 5, 8; XV. 3 - 5; XVI. 8-11, 13-19,21-22;

XVII, 7 -11.

(6) If the material before exposure to the air has been heated to redness for some time, then if it be exposed to the air for a considerable length of time dried in a des~~s~~icator, its weight is found to be that of a corresponding mixture of BaB_2O_4 and $BaCO_3$.

IX, 17-33, 50-56,; X 16-32, 49-55;

XI, 15-20; XIII, 10-11; XV, 6-7.

(7) If the weight of the material has been carried below the theoretical by heating, this weight is re~~assumed~~gained upon heating at 450° - 470°, and we find after such heating that the

weight is that of a mixture of $BaB_2O_4 + BaCO_3$

XVI, 35-38; 39-41;

XVIII, 13-16; XIX, 2-3.

(8) Or if after the weight has been carried below the theoretical the material is first allowed to saturate itself in the air, then upon heating to 450°-470°, theoretical weight is obtained

XVI, 12-20, 24-27. XVII, 12-13;

XVIII, 11-12, XIX, 2-4.

(9) Closest agreement between the weight found and the theoretical is gotten when the material is heated to 450°-470° and allowed to cool in the air.

XVI, 42-47; XIX, 8.

Conclusions:-

We have to deal in this investigation with the distribution of barium between the two acids, carbonic and boric. Inasmuch as it adds simplicity and clearness to the reactions and explanations, the salts are expressed in dualistic formulae: hence, in these terms, we have to deal with the distribution of the basic oxide BaO, between the two acid oxides CO_2 and B_2O_3. The quantity of BaO, and of B_2O_3 in any mixtureof salts studied remain constant; that of CO_2 varies.

The neutral salts of boric acid are referred to the "normal"

acid H_3BO_3; "the acid salts" referred to in this work are those containing relatively more acid to base than do the normal salts Thus:

H_3BO_3		$(H_2O)_3B_2O_3$	$(BaO)_3B_2O_3$
$H_4B_2O_5 = 2H_3BO_3 - H_2O$	=	$(H_2O)_2 \cdot B_2O_3$	$(BaO)_2 \cdot B_2O_3$
$HBO_2 = H_3BO_3 - H_2O$	=	$H_2O.B_2O_3$	$BaO.B_2O_3$
$H_2B_4O_7 = 4H_3BO_3 - 5H_2O$	=	$H_2O.(B_2O_3)_2$	$BaO.(B_2O_3)_2$
$H_2B_6O_{10} = 6H_3BO_3 - 8H_2O$	=	$H_2O.(B_2O_3)_3$	$BaO.(B_2O_3)_3$
etc.		etc.	etc.

In the determinations in Part II, we begin by running boric acid into an excess of barium hydroxide solution. An experiment, already quoted from Berg, shows that the borates at first precipitated dissolve more or less completely in the excess of barium hydroxide, when it is present. Thus we get salts containing more than one equivalent of base to one of acid. On passing carbon dioxide to neutral reaction this formation of borates less acid than the metaborate is reversed and more acid borates and barium carbonate result. Upon evaporation we find the weight of the mixed salts to exceed that for a corresponding mixture of barium metaborate and barium carbonate. A general formula may make this clearer. We may represent the mixture of barium metaborate and carbonate thus.

$$m\,(BaO.\,CO_2) + n\,(BaO.B_2O_3)$$

The passage of CO_2 has left a mixture weighing more than this and containing more acid borates and barium carbonate, thus

$$m(BaO.CO_2) + x(BaO.CO_2) + (BaO)_{(n-x)}.(B_2O_3)_n.$$

This mixture when ~~upon~~ heated ~~ing~~ is found to lose weight and if the heating be strong enough, the loss in weight is so great that the weight of the mixed salts falls below that for a mixture of barium metaborate and carbonate. The losses in weight are due to the action of the more acid borates on barium carbonate, driving out carbon dioxide and forming borates not so acid. If the heating be strong enough the borates formed become less acid than the metaborate, and we then find deficits in weight as compared with that of a mixture of metaborate and carbonate. General formulae may aid again:-

After evaporation, and before heating we had:-

$$m(BaO.CO_2) + x(BaO.CO_2) + (BaO)_{(n-x)}.(B_2O_3)_n$$

Gentle heating causes some losses in weight; we may represent, thus

$$m(BaO.CO_2) + (x-y)(BaO.CO_2)+(BaO)_{n-(x-y)}.(B_2O_3)_n$$

The simplest case is where y just equals x, restoring the condition of metaborate and carbonate; thus,

$m(BaO.CO_2) + n(BaO.B_2O_3)$, carbon dioxide is escaping.

If the heating is strong enough, borates less acid than the metaborate are formed and the weight becomes less than that of a mixture of metaborate and carbonate; thus

$m-x(BaO.CO_2) + (BaO)_{(n+x)}(B_2O_3)_n + xCO_2$, the escape of this xCO_2 is the cause of deficits in weight.

If a mixture of salts in which, as the result of heating, all the borates more acid than the metaborate have been converted into those less acid than it, is exposed to the carbon dioxide of the air at the room temperature or is heated to 450°C - 470°C (CO_2 from combustion of gas in burners of course being present,) then the less acid borates are attacked by the CO_2 and are converted into barium metaborate and carbonate: thus

$$m-x(BaO.CO_2) + (BaO)_{n+x} \cdot (B_2O_3)_n + xCO_2$$
$$= m(BaO.CO_2) + n(BaO.B_2O_3)$$

This explanation accounts for all the facts observed in this investigation and by Jones when working under similar conditions. It is also not at variance with what is known of the character and behavior of boric acid. As early as 1842, it was pointed out by Schaffgotsch*, that the base in such compounds as $CaCO_3$, $SrCO_3$, $BaCO_3$, $LiCO_3$, Na_2CO_3, $KHCO_3$, $NaNO_3$, KNO_3 and BaN_2O_6 could be quantitatively determined by fusing them with borax,- the boric acid completely expelling the carbonic and nitric acids.

The reverse reaction, that is the reassumption of CO_2 at lower temperatures by a mixture similar to those we have dealt with, was observed by Rose*[(1)]. He brought together solutions of Na_2CO_3 and B_2O_3; after evaporation he heated to a high temperature getting constant weight; but when the material was sub-

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* Poggendorff's Annalen 57, p.263.

1 " " 80, p. 262.

sequently heated to a lower temperature, it took on again some of the CO_2 it had lost by strong heating. Some oxides, he says, acting on alkaline carbonates drive out a definite amount of CO_2; But B_2O_3 is different, the amount of CO_2 driven out depending on the temperature and length of heating.

The similarity of these reactions to those studied is apparent.

PART III.

For the question in hand Parts I and II have suggested a satisfactory explanation. Part III tests this explanation.

The condition of most stable equilibrium in the system under study seems to be when the mixture consists of barium metaborate and barium carbonate. Such a mixture is obtained in Part II by proper treatment of mixtures of barium carbonate and other borates. This condition of equilibrium is destroyed by heating and restored by the action of carbon dioxide.

The character of the salts in the mixtures studied in Part II has been inferred from the weights of the mixtures. To prepare barium metaborate and subject it to similar treatment when by itself, to do the same by barium carbonate, and then to mix and subject the mixture of the two to the same treatment as the separate salts is the plan of Part III. The explanation offered in Part II suggests that neither salt should be affected when heated alone in carbon dioxide, air, etc.; but that on <u>strongly</u> heating a mixture of the two, carbon dioxide should be given off due to reactions analogous to this:-

$$BaO.CO_2 + BaO.B_2O_3 = 2BaO.B_2O_3 + CO_2.$$

Upon allowing carbon dioxide to act upon a mixture which has undergone such reactions, carbon dioxide should be absorbed until the condition of equilibrium is reestablished by reactions analogous to this

$$2BaO.B_2O_3 + CO_2 = BaO.CO_2 + BaO.B_2O_3$$

Barium metaborate was prepared as directed by Berg. Equivalent aqueous solutions of boric acid and barium hydroxide were prepared and the former poured into the latter. (This order is advised, upon the ground of experiences with mixtures made in both ways.) A precipitate settled out, which was dissolved by bubbling steam into the liquid. To remove a slight cloudiness that remained, which was probably $BaCO_3$, the solution was filtered in an atmosphere free from carbon dioxide. To a portion of the filtered solution an equal volume of 95% was gradually added with constant shaking. (This order should be followed; to add the solution to the alcohol is less satisfactory.) The precipitate formed was allowed to stand in the solution and at the end of twenty-four hours it had become fairly crystalline. Seventy-two hours were allowed for complete crystallization. The crystals were then removed and quickly washed in cold water, and dried in the air by rubbing them upon an unglazed porcelain plate. Another portion of the filtered solution was set aside, without the addition of alcohol. In a weeks time the bottom of the bottle in which it was kept was studded with wart-like crystals. The lower surfaces of these hemispheres were very firmly attached to the glass; they exhibited a radiate structure. Analyses proved this salt identical with that gotten by the addition of alcohol to the other portion of the same solution; it was $BaB_2O_4 + 5\,H_2O$

Comparison with Berg's article shows that the salt obtained differed from his by one molecule of water, his being

$BaB_2O_4 + 4H_2O$.

Determinations of water crystallization were made by heating the salt in a platinum boat in a combustion tube, up to a red heat. The percentage of water for $BaB_2O_4 + 5H_2O$ is 28.74%, while for Berg's salt, $BaB_2O_4 + 4H_2O$, it is 24.39%.

Percentage of water found = 28.97%

= 28.89%

In the latter determination .9778g of the salt had been used. It was allowed to remain in the boat, after dehydration, and was studied under varied conditions. The experiments are recorded in the table:-

	Weight found in grams.	Change in wt. in grams.
1 Heated in dry air from which CO_2 was removed	.6955	-.2823
2 Heated in dry air from which CO_2 was removed	.6943	-.0012
3 Heated in dry air from which CO_2 was removed	.6940	-.0003
4 Heated in dry air from which CO_2 was removed	.6940	± 0
5 Heated in dry air from which CO_2 was removed	.6936	-.0004
6 Heated to redness in dry CO_2 for 2 hours	.6945	+.0009
7 Heated to redness in dry CO_2 for 2 hours	.6948	+.0003
8 Heated to lower temperature in dry CO_2 for 2 hours	.6951	+.0003

	Weight found in grams	Change in wt. in grams
9 Heated to lower temperature in dry CO_2 for 1 1/2 hours	.6950	-.0001
10 Heated to lower temperature in dry CO_2 for 1 hour	.6947	-.0003
11 Heated to lower temperature in moist CO_2 for 2 hours	.6954	+.0007
12 Heated to lower temperature in moist CO_2 for 2 hours	.6948	-.0006
13 Heated to redness in moist CO_2 for 2 hours	.6937	-.0011
14 Heated to redness in moist CO_2 for 2 hours	.6937	$\pm$ 0
15 Stood in air 1 hours	.6941	+.0004
16 Stood in air 2 hours	.6940	-.0001
17 Stood in air 3 1/4 hours	.6941	+.0001
18 Stood in air 4 1/4 hours	.6942	+.0001
19 Stood in air 18 1/4 hours	.6944	+.0002

On the basis of these experiments the metaborate was regarded as stable under the same conditions as were used in the determinations in Part II.

Before using this barium metaborate, portions of it were analyzed. This was accomplished by first fusing with double carbonate of sodium and potassium, dissolving the melt in water and washing the $BaCO_3$, drying and weighing. This $BaCO_3$ was then dissolved in dilute HCl, the solution diluted and Ba precipitated as $BaSO_4$ in the usual way. The carbonate of Ba was im-

pure, as was indicated both by its weight and by the material left in suspension when it was dissolved in H C l; the solution had to be filtered before H S O was added.

I	.2072	.1866	.1450	69.96%	.2142	.1407	67.92%	68.7%
II	.1897	.1718	.1335	70.39%	.1969	.1294	69.19%	

The passage through $BaCO_3$ was made because there was doubt of the completeness of precipitation of B a as $BaSO_4$ in the presence of boric acid.

Pure B a C O was subjected to similar treatment to that of the B a B O .

Experiment	Weight found in grams	Change in wt. in grams
	6.3476	
Heated at red heat over bunsen burner for 1/2 hours	6.3340	-.0136
Heated at red heat over bunsen burner for 1/2 hour	6.3341	+.0001
Heated at red heat over bunsen burner for 1/2 hour	6.3342	+.0001
Material put in a platinum boat	4.2059	
Heated at red heat in dry C O for 2 hrs.	4.2057	-.0002
Heated at low temp. in dry C O for 2 hours	4.2053	-.0004

B a C O_3 like B a B_2O_4 is stable inder these conditions.

In weighing, the boat containing the materials studied was enclosed in a glass stoppered weighing tube to prevent access of the moisture and carbon dioxide of the air.

Having studied the B a B_2O_4 and B a C O_3 separately, it yet remained to study the behavior of a mixture of the two under varied conditions.

Equivalent quantities were taken from the specimens of B a B_2O_4 and B a C O_3 whose behavior had just been tested as described. They were thoroughly mixed in a large platinum dish during an hour and a quarter. A weighed quantity of this mixture was introduced into a platinum boat and its behavior studied in a combustion tube as recorded in the table that follows:-

					Weight found in grams	Change in wt. in grams	Error in grams
–					1.2839		
1	Stood over H_2SO_4 over night				1.2836	-.0003	
2	2 hrs.	gentle heat	air less C O_2	dry	1.2822	-.0014	
3	"	"	"		1.2821	-.0001	
4	2 1/2 hrs.	to softening temp. of glass	"		1.1932	-.0889	-.0889
5	2 hrs.	"	"		1.1923	-.0009	-.0898
6	2 hr.	low temp.	C O_2		1.1932	+.0009	-.0889

7	1 hr.	temp. of room	CO_2	dry	1.1934	+.0002	-.0887
8	"	medium temp.	"	"	1.1987	+.0053	-.0834
9	"	"	"	"	1.1996	+.0009	-.0825
10	"	slightly higher temp.	"	"	1.2117	+.0121	-.0704
11	"	"	"	"	1.2252	+.0135	-.0569
12	3 hr.	"	"	"	1.2342	+.0090	-.0479
13	1 hr.	"	"	"	1.2404	+.0062	-.0417
14	1 hr.	"	"	"	1.2442	+.0038	-.0379
15	1 hr.	"	"	"	1.2461	+.0019	-.0360
16	4 hrs.	"	"	"	1.2558	+.0097	-.0263
17	9 hrs.	"	"	"	1.2639	+.0081	-.0182
18	1 hr.	"	"	"	1.2647	+.0008	-.0174
19	3 1/2 hrs.	"	"	"	1.2675	+.0028	-.0146
20	4 3/4 hrs.	"	"	"	1.2696	+.0021	-.0125
21	3 hrs.	"	"	"	1.2709	+.0015	-.0112
22	4 hrs.	"	"	"	1.2766	+.0057	-.0055
23	2 1/2hrs.	"	"	"	1.2785	+.0019	-.0036
24	5 hrs.	"	"	"	1.2794	+.0009	-.0027
25	2 1/2hrs.	"	"	"	1.2803	+.0009	-.0018
26	5 hrs.	"	"	"	1.2810	+.0007	-.0011
27	2 3/4hrs.	"	"	"	1.2812	+.0002	-.0009
28	5 1/4hrs.	"	"	"	1.2813	+.0001	-.0008
29	3 hrs.	"	"	"	1.2819	+.0006	-.0002
30	5 hrs.	"	"	"	1.2823	+.0004	+.0002
31	2 1/2hrs.	"	"	"	1.2825	+.0002	+.0004
32	3 hrs.	"	"	"	1.2829	+.0004	-.0008

33	5 hrs.	slightly higher temp.	C O_2	dry	1.2845	+.0016	+.0024
34	8 hrs.	"	"	"	1.2828	-.0017	+.0007
35	8 1/4hrs.	"	"	"	1.2833	+.0005	+.0012
36	7 hrs.	red heat	"	"	1.2335	-.0498	-.0486
37	8 hrs.	"	"	"	1.2185	-.0150	-.0636
38	"	"	"	"	1.2192	+.0007	-.0629
39	"	"	"	"	1.1964	-.0228	-.0857
40	7 hrs	"	"	"	1.1908	-.0056	-.0913
41	8 hrs.	"	"	"	1.1865	-.0043	-.0956
42	"	"	"	moist	1.2151	+.0286	-.0670
43	"	"	"	"	1.2155	+.0004	-.0666
44	"	"	air less C O_2	dry	1.1860	-.0295	-.0961
45	"	"	C O_2	moist	1.1866	+.0006	-.0955
46	"	lower temp.	"	"	1.2120	+.0254	-.0701
47	"	"	"	"	1.2115	-.0005	-.0706
48	"	temp. of room	"	"	1.2146	.0031	-.0675
49	7 1/2hrs.	medium temp.	"	"	1.2130	-.0016	-.0691
50 50	"	slightly more elevated temp	"	"	1.2491	+.0361	-.0330
51	8 hrs.	"	"	"	1.2541	+.0050	-.0280
52	"	"	"	"	1.2510	-.0031	-.0311
53	"	higher temp.	"	"	1.2593	+.0083	-.0228
54	"	" "	"	"	1.2424	-.0169	-.0397
55	"	"	"	"	1.2646	+.0222	-.0175

In experiments 4 and 5, a weighed set of absorption tubes such as are used in an organic analysis for C and H was attached to the combustion tube in which the boat and mixture were heated. The increase in weight of the Geissler bulbs indicated that the weight lost by the mixture in the boat was CO_2. The loss in weight in 1, 2 and 3 was regarded as water which had deposited from the air on the particles of the BaB_2O_4 and $BaCO_3$ while they were being thoroughly mixed.

Conclusions:-

That the conclusions of Part II are correct is confirmed by Part III. When an "acid borate" of barium like the metaborate, is heated strongly with barium carbinate reaction takes place, less acid borates being formed and carbon dioxide being expelled. When such a less acid borate is exposed to the action of carbon dioxide, it may take up as much carbon dioxide as it had lost, forming again the original borate and carbonate.

Thus, in the case studied the total weight of CO_2 contained originally in the boat before heating was $.1356^g$ which was all present as $BaCO_3$. Strong heating of the mixture caused a loss of carbon dioxide of $.0898^g$ and this is almost exactly 2/3 of the total CO_2 originally present. The difference being

$.0904 - .0898 = .0006^g$.

Hence during the heating this reaction has taken place.

$3\,(BaO.\,CO_2) + 3\,(BaO.\,B_2O_3) = 5\,BaO.3\,B_2O_3 + BaO.CO_2 + 2\,CO_2$

When stability is again reached after heating in carbon dioxide, experiments 32 - 35, we had the weight again of the original mixture. Therefore the reverse of the former reaction has occurred

$5 (BaO.3 B_2O_3 + BaO.CO_2 + 2 CO_2 = 3(BaO.B_2O_3)+3(BaO.CO_2)$

In experiments 42 and 43, and also in experiments 46 to 49, the material in the boat seems to be at or very near another point or condition of stability. An average of the amounts by which the mixture differs from its original weight proves to be 68 milligrams and this is almost exactly half of the total C O originally present. Therefore this salt has been formed

$3 BaO. 2 B_3O_3$ involving the reaction:

$$2(BaO. CO_2) + 2 (BaO. B_2O_3) = 3 BaO.2 B_2O_3 + BaOCO_2 + CO_2$$

The behavior in experiments 44 and 45 where the material gains 29 milligrams in eight hours and retains it while heated for eight hours longer under conditions presumably more favorable to its decomposition, it seems justifiable to assume some stable salt as formed. 96 milligrams is almost exactly 5/7 of the total CO_2 present originally. Therefore this reaction has taken place in passing from experiment 35 - 45.

$$7 (BaO. CO_2) + 7(BaO.B_2O_3) = 12 BaO.7 B_2O_3 + 2 BaCO_2 + 5 CO_2$$

The quantity of [illegible] escaping [illegible] dination, [illegible] on [illegible] [illegible]. Therefore the [illegible] of the [illegible] has occurred

[illegible]

In experiments 42 and 43, and also in experiments [illegible] 40, the [illegible] in the [illegible] point or condition of stability. [illegible] of the [illegible] by which the [illegible] differs from its original [illegible] be [illegible] and this is almost exactly half of the [illegible] C O originally present. Therefore this [illegible]

[illegible] involving the reaction

[illegible]

The behavior in experiments 44 and 45 [illegible] in eight hours and [illegible] this [illegible] conditions [illegible] is the decomposition, if [illegible] is [illegible]. [illegible] of the total C O present originally. [illegible] has taken place in [illegible] the experiment [illegible]

[illegible]

Summary of Conclusions of Parts I,II, and III.

When boric acid in aqueous or alcoholic solution is introduced into an excess of aqueous barium hydroxide solution and then carbon dioxide is passed to neutral reaction toward phenolphthalein, during subsequent evaporation of the water or very dilute alcohol, little or no boric acid is lost.

After evaporation, the weight of the mixed salts is always greater than the weight of mixture of barium metaborate and barium carbonate containing the same weight of boric acid and of barium; this excess weight is brought about by the action of carbon dioxide which, beside precipitating the excess of barium hydroxide as carbonate, attacks the borates present - which contain at this point more base in proportion in proportion to acid than does the metaborate - , taking from them barium oxide to form carbonate, and forcing the boric acid into combinations more acid than the metaborate.

Upon heating this mixture of metaborate and carbonate interaction between the more acid borates and barium carbonate takes place, carbon dioxide being expelled and less acid borates resulting; this displacement of carbon dioxide causes loss in weight. The extent to which this interaction goes, is determined by the length and intensity of the heating to which the mixture is subjected. That the more acid borates may be completely converted by this interaction into borates less acid than the metaborate requires strong heating over a bunsen burner; when this has been accomplished the mixed salts weigh less than an equivalent mixture of metaborate and carbonate.

These losses in weight may be recovered by the action of carbon dioxide. If it acts in the presence of water and phenol-phthalein then after evaporation, the mixed salts again weigh more than an equivalent mixture of metaborate and carbonate for the reason given above. If the carbon dioxide of the air is allowed to act on a mixture of borates less acid than the metaborate with barium carbonate, the less acid borates are converted into metaborate the barium oxide thus freed being converted into barium carbonate. If the carbon dioxide acts at approximately 450° - 470°, the same result is accomplished. The weight of the mixed salts is then, of course, that of an equivalent mixture of metaborate and carbonate.

When a mixture of barium metaborate and barium carbonate is heated strongly, interaction takes place and carbon dioxide is expelled. The losses in weight can be restored by any of the above methods.

BIOGRAPHICAL.

David Wilbur Horn was born May 7, 1877, at Carlisle, Pennsylvania. His early education was received at his home and at the public schools of that town. After his fifth year in these schools, he withdrew from the high school to enter Dickinson Preparatory School, also at Carlisle. Completing the three year course he entered Dickinson College and in the summer of 1897 was graduated with the degree of A. B. In 1898 the degree of A. M. was conferred by the same institution. Since the fall of 1897 he has been a graduate student in Chemistry, Geology and Physics in Johns Hopkins University. In January, 1900, he was appointed a University scholar in Chemistry.